European Commission

ERM
European Reference Materials

CERTIFICATION REPORT

The Certification of the Mass Fractions of As, Br, Cd, Cr, Hg, Pb, S, Sb, Sn and Zn in Low-Density Polyethylene: ERM®-EC680m

EUR 27572- 2015

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)

Contact information
Reference materials sales
Address: Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium
E-mail: jrc-irmm-rm-distribution@ec.europa.eu
Tel.: +32 (0)14 571 705

JRC Science Hub
https://ec.europa.eu/jrc

JRC98613

EUR 27572 EN

ISBN 978-92-79-53800-1 (PDF)
ISSN 1831-9424 (online)
doi:10.2787/255735

Luxembourg: Publications Office of the European Union, 2015

Printed in Belgium

Abstract
This report describes the production of ERM-EC680m, a low-density polyethylene (LDPE) material certified for the mass fraction of elements. The material was produced following ISO Guide 34:2009.
An LDPE material containing certain elements was prepared from commercially sourced low-density polyethylene and organic and inorganic pigments. The material was extruded, mixed and filled into bottles.
Between-bottle homogeneity was quantified and stability during dispatch and storage were assessed following with ISO Guide 35:2006. The within-unit homogeneity was quantified to determine the minimum sample intake.
The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, instability and characterisation.
The material is intended for the quality control and/or assessment of method performance. As any reference material, it can also be used for control charts, validation studies or calibration of methods. The CRM is available in glass bottles containing 100 g of polyethylene granulate. The minimum amount of sample to be used is 150 mg for the determination of Cl and 50 mg for the determination of all other elements.
The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

CERTIFICATION REPORT

The Certification of the Mass Fractions of As, Br, Cd, Cr, Hg, Pb, S, Sb, Sn and Zn in Low-Density Polyethylene: ERM®-EC680m

Raquel Sanchez Romero, Thomas P.J. Linsinger

European Commission, Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Geel, Belgium

Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM-EC680m, a low-density polyethylene (LDPE) material certified for the mass fraction of elements. The material was produced following ISO Guide 34:2009 [1].

An LDPE material containing certain elements was prepared from commercially sourced low-density polyethylene and organic and inorganic pigments. The material was extruded, mixed and filled into bottles.

Between-bottle homogeneity was quantified and stability during dispatch and storage were assessed following with ISO Guide 35:2006 [2]. The within-unit homogeneity was quantified to determine the minimum sample intake.

The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and include uncertainties related to possible inhomogeneity, instability and characterisation.

The material is intended for the quality control and/or assessment of method performance. As any reference material, it can also be used for control charts, validation studies or calibration of methods. The CRM is available in glass bottles containing 100 g of polyethylene granulate. The minimum amount of sample to be used is 150 mg for the determination of Cl and 50 mg for the determination of all other elements.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following certified values were assigned:

	Mass fraction	
	Certified value [1)] [mg/kg]	Uncertainty [2)] [mg/kg]
As	4.7	0.4
Br	181	9
Cd	20.8	0.9
Cr	9.6	0.5
Hg	2.56	0.16
Pb	11.3	0.4
S	86	9
Sb	9.6	0.7
Sn	20.7	1.6
Zn	194	12

1) Certified values are values that fulfil the highest standards of accuracy. The given value(s) represent(s) the unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of units (SI).

2) The uncertainty is the expanded uncertainty of the certified value with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

In addition to the certified values, an indicative value for Cl of 84 ± 11 mg/kg (expanded uncertainty with k=2 corresponding to a level of confidence of about 95 %) was assigned.

Table of contents

Glossary

AES	Atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CI	Confidence interval
CRM	Certified reference material
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
DMA	Direct mercury analyser
EC	European Commission
EDXRF	Energy-dispersive x-ray spectrometry
ERM®	Trademark of European Reference Materials
EU	European Union
ETAAS	Electrothermal atomic absorption spectrometry
GUM	Guide to the Expression of Uncertainty in Measurements [3]
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-QMS	ICP-Quadrupole mass spectrometry
ICP-SFMS	ICP-Sector field mass spectrometry
ID	Isotope dilution
IR	Infrared
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0NAA	k_0-Neutron activation analysis
k_2'	Factor for the two-sided 95 % tolerance limits for a normal distribution
LDPE	Low-density polyethylene
LOD	Limit of detection
$\overline{m}$	Average mass used during the minimum-sample intake measurements
m_{min}	Minimum sample mass representative for the whole bottle
$MS_{between}$	Mean of squares between-bottle from an ANOVA
MS_{within}	Mean of squares within-bottle from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
NIST	US National Institute of Standards and Technology
rel	Index denoting relative figures (uncertainties etc.)
QCM	Quality control material
RM	Reference material
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added if appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added if appropriate
se	Standard error
SI	International System of Units

$s_{m,rel}$	Relative standard deviation obtained in the minimum sample intake study
s_{wb}	Within-unit standard deviation; an additional index "rel" is added if appropriate
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added if appropriate
T	Temperature
t	Time
t_i	Time point for each replicate
t_{sl}	Proposed shelf life
u	Standard uncertainty
U	Expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added if appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added if appropriate
u_{char}	Standard uncertainty related to the material characterisation; an additional index "rel" is added if appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added if appropriate
U_{CRM}	Expanded uncertainty related to the certified value; an additional index "rel" is added if appropriate
u_{lts}	Standard uncertainty related to the long-term stability; an additional index "rel" is added if appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added if appropriate
u_t	Standard uncertainty of trueness
$u_{target,rel}$	Maximum relative uncertainty acceptable for sub sampling
UV	Ultraviolet
$\overline{x}$	Arithmetic mean
$\overline{x}_{ns}$	Arithmetic mean of all results of normal stock samples
$\overline{x}_{ref}$	Arithmetic mean of results of reference samples
α	Significance level
$\nu_{MSwithin}$	Degrees of freedom of $\nu_{MS\text{within}}$

1 Introduction

1.1 Background

Protection of the environment and human health from excessive heavy metal loads is an important goal for regulators. To achieve this, the European Union has passed legislation to limit the load of certain elements in various products, amongst them Directive 94/62/EC (packaging directive) [4], Directive 2011/65/EU (restriction of the use of certain hazardous substances in electric and electronic equipment) [5] and Directive 2000/53/EC (end of live vehicles) [6].

- Directive 94/62/EC concerns plastics packaging and packaging material and regulates the amounts of Cd, Cr, Hg and Pb in plastics used for packaging. Article 11 of this Directive states that the sum of Pb, Cd, Hg and Cr(VI) must be below 100 mg/kg as of June 30, 2001.
- Directive 2011/65/EU ("RoHS 2") aims at reducing the amount of hazardous substances in electric and electronic equipment. Use of Pb, Hg, Cr(VI), Cd and polybrominated flame retardants is prohibited unless no alternatives exist for certain applications. In addition to the sum, maximum limits for Pb, Hg and Cr (VI) (1 g/kg) and Cd (100 mg/kg) in homogeneous materials are set. This directive also sets upper limits for the mass fractions of of polybrominated flame retardants. Measurement of total Br is often used as screening for these compounds. Legislation similar to 2011/65/EU exist, amongst others, in the People's Republic of China, Japan, the Republic of Korea, Turkey and some states of the USA (e.g. California).
- Similarly, Directive 2000/53/EC aims at reducing the amount of hazardous substances entering the environment from old vehicles. As in Directive 2011/65/EU, Council Decision 2005/673/EC [7] sets maximum limits of 1 g/kg in homogeneous materials for Pb, Hg, Cr(VI) and 0.1 g/kg for Cd.
- Cl, S, Sb and Sn are not regulated, but as they are volatile elements and CRMs for these elements are scarce, certification is desirable as well. This assessment was confirmed in a survey of users of BCR-680 and BCR-681.

In support of these directives, several certified reference materials (CRMs) have been produced by the European Commission, namely a set of four polyethylene materials (on behalf of the German Verband der Automobilindustrie e.V., Frankfurt) [8] and two additional high-density polyethylene materials, BCR-680 and BCR-681 [9]. BCR-680 and BCR-681 were re-branded as ERM-EC680 and ERM-EC681 in 2004. These materials were exhausted in 2006 and two replacement batches (ERM-EC680k and ERM-EC681k) consisting of low-density polyethylene (LDPE) were released in 2007. This report describes the production of ERM-EC680m, the replacement batch of ERM-EC680k.

1.2 Choice of the material

As the new material should be a close replacement of the previous one, it was decided to use LDPE again as matrix with similar element levels as the previous batch, ERM-EC680k. As for the pigments used, some changes were introduced: ERM-EC680k contained Cr_2O_3 and SnO_2, which are virtually not digestible by acid digestion methods, so they were replaced by pigments also accessible for wet-chemistry methods. In addition, pigments were also selected according to commercial availability. Therefore, $PbCrCrO_4/PbSO_4$ was replaced by Pb_3O_4 and $CaCrO_4$.

1.3 Design of the project

The goal was to produce a CRM similar to ERM-EC680k.

After the processing, homogeneity was assessed via an experimental homogeneity study. The stability of the material was based on information on the stability of the matrix and pigments, the stability of the previous batches and a limited stability study of the material itself.

The characterisation was based on an intercomparison involving expert laboratories with demonstrated competence in the determination of trace elements. Care was taken to select combinations of different sample preparation/quantification techniques to demonstrate the absence of a significant method bias.

The data of the characterisation study were subjected to a technical and statistical evaluation and certified values were assigned.

2 Participants

2.1 Project management and data evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

AIMPLAS-Instituto Tecnológico del Plástico, Valencia, Spain

2.3 Homogeneity study

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

Technische Universität Bergakademie Freiberg, Freiberg, Germany

2.4 Stability study

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

2.5 Characterisation

ALS Scandinavia AB, Luleå, Sweden
(measurements for one method under the scope of ISO/IEC 17025 accreditation SWEDAC 2030)

Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

Bundesanstalt für Materialforschung und -Prüfung, Berlin, Germany
(measurements under the scope of ISO/IEC 17025 accreditation DAkks D-PL-11075-14-00)

ECN, Petten,The Netherlands

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

Institut Jožef Stefan, Ljubljana, Slovenia
(measurements under the scope of ISO/IEC 17025 accreditation SLOVENSKA AKREDITACIJA LP090)

Metropolilab, Helsinki, Finland
(measurements under the scope of ISO/IEC 17025 accreditation FINAS T058)

SCK.CEN Studiecentrum voor Kernenergie, Mol, Belgium
(measurements under the scope of ISO/IEC 17025 accreditation BELAC 15-TEST)

Solvias AG, Kaiseraugst, Switzerland

Umweltbundesamt GmbH, Wien, Austria
(measurements under the scope of ISO/IEC 17025 accreditation Akkreditierung Austria ID 200)

Università Degli Studi di Ferrara, Ferrara, Italy

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

3 Material processing and process control

3.1 Origin and purity of the starting material

The material was prepared from general purpose grade LDPE and the inorganic pigments shown in Table 1.

Table 1: Pigments used for the production of ERM-EC680m. Purity values given are as specified by the supplier of the pigments.

Compound	Pigment name	Purity [%]	Comment
As_2O_3	Arsenic trioxide	>99	Same as used in the production of ERM-EC680k
$C_{32}Br_6Cl_{10}CuN_8$	Pigment Green 36; Heliogen Green L9361	95	Same as used in the production of ERM-EC680k
$C_{32}Cl_{16}CuN_8$	Pigment Green 7; Heliogen Green L8735	95	Same as used in the production of ERM-EC680k
HgS	Pigment Red 106; Vermilion	99	Same as used in the production of ERM-EC680k
Sb_2O_3	Pigment White 11	98	Same as used in the production of ERM-EC680k
CdS	Pigment Yellow 37	98	A mixture of CdS/ZnS (Pigment Yellow 35) was used in the production of ERM-EC680k
ZnS	Pigment White 7; Sactolith HDS	98	
SnS_2	Pigment Yellow 38	98	Not used in the production of ERM-EC680k
Pb_3O_4	Pigment Red 105	96	Not used in the production of ERM-EC680k
$CaCrO_4$	Pigment Yellow 33	95	Not used in the production of ERM-EC680k

3.2 Processing

3.2.1 Processing of the plastic

A preliminary particle size determination showed that the median diameter (D_{50}) of all pigments was about 10 μm. During the production of BCR-680 it was found that particle sizes of 1 μm and below are required to ensure good repeatability even at low sample intakes [9].

Therefore, the pigments were dry-mixed in the appropriate portions for each intermediate batch (see below) in a turbomixer and jet-milled to a median particle size (D_{50}) of 1 µm.

An intermediate batch of high element mass fractions was prepared by mixing the milled pigments with pure LDPE (EXCEED LL6161RQ, Exxon Mobil Chemical) in a co-rotating twin screw extruder using a very high shear screw design to ensure a good dispersion of the pigments. The obtained material was cooled in a water bath and cut into 3 x 3 mm pellets.

This intermediate product was diluted in a ratio 1:50with pure LDPE (LLDPE M200024, Sabic), which does not contain any plasticisers. This dilution was performed using a co-rotating twin screw extruder and gravimetric feeders to mix the fresh LDPE and the intermediate batch. The obtained material was cooled in a water bath and cut into 3 x 3 mm pellets.

Before preparation of the final batch, a test batch of 75 kg was prepared and samples were taken every 45 min (five samples in total). The samples were analysed for their trace element content by electron-dispersive x-ray spectrometry and were found homogeneous. The trace element distribution in the samples was investigated by scanning electron microscopy coupled with X-ray detection. These tests (

Figure 1) showed the good dispersion of the pigments and the absence of agglomerates. These tests also confirmed the control of the preparation process and it was decided to proceed with the processing of the final batch. In total, 600 kg of the final batch were produced according to the procedure above.

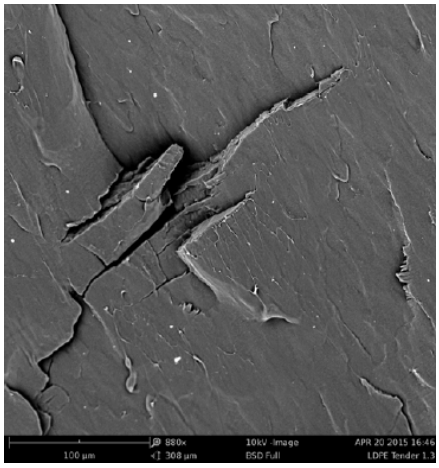


Figure 1: Representative scanning electron microscope image of ERM-EC680m. The white spots are the inorganic pigments; scale bar is 100 µm.

3.2.2 Mixing and bottling

The batch was split into two sub-batches of 300 kg and each sub-batch was mixed for 2 h in a three-dimensional mixer. Each sub-batch was again split into two, one-half of sub-batch 1 was combined with one-half of sub-batch 2 and mixed again for 2 h. This process was repeated once. The mixing scheme for ERM-EC680m is given in Figure 2.

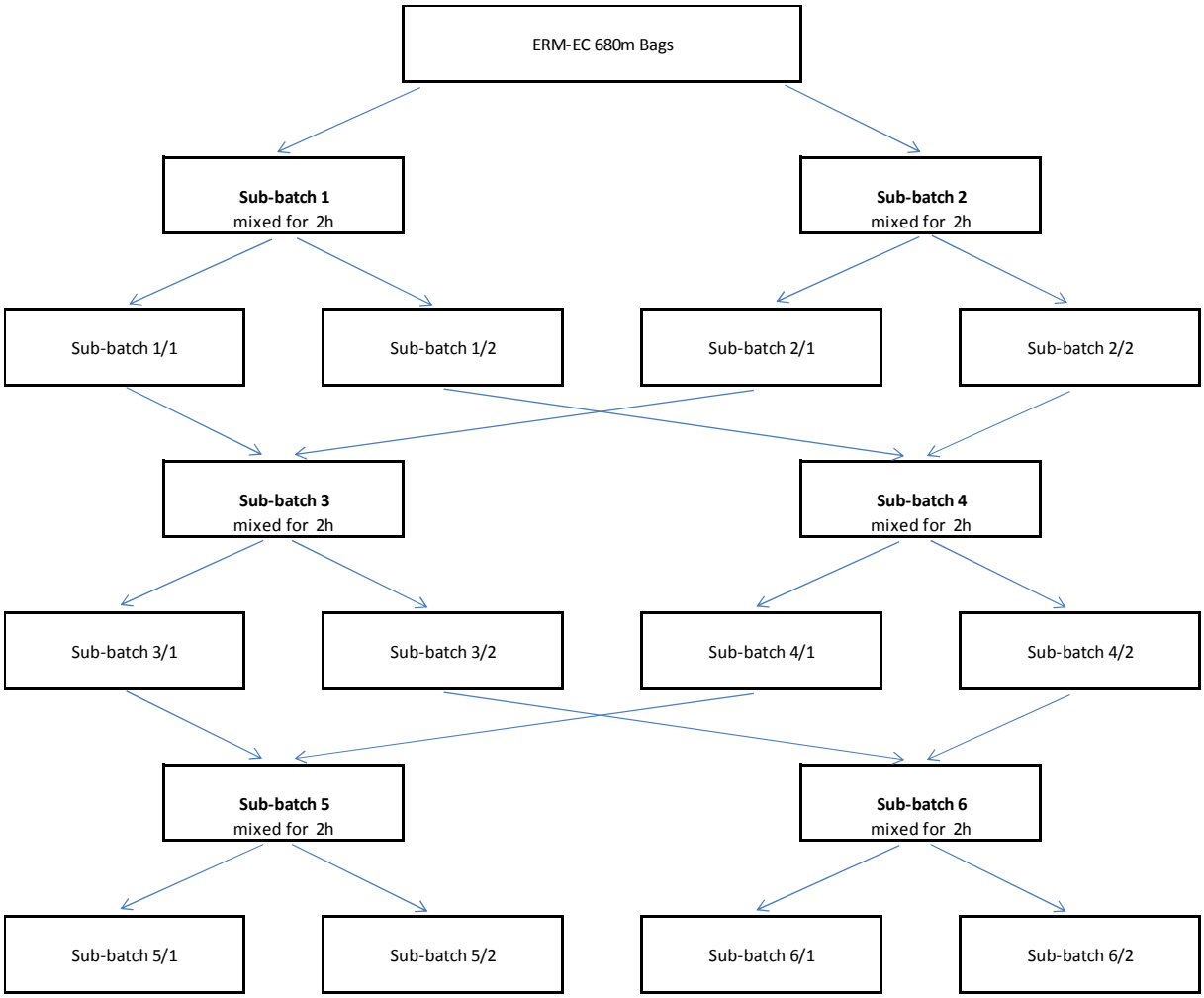


Figure 2: Mixing of ERM-EC680m

The final material from each sub-batch was filled into amber brown bottles containing 100 g granulate each. The bottles were labelled in the filling sequence.

4 Homogeneity

An essential requirement for any reference material is the equivalence between the material in the various bottles. In this respect, it is relevant whether the variation between bottles is significant compared to the uncertainty of the certified value. Contrastingly, it is not relevant if this variation between bottles is significant compared to the analytical variation. Consequently, ISO Guide 34 requires RM producers to quantify the between bottle variation. This aspect is covered in between-bottle homogeneity studies.

The within-bottle inhomogeneity determines the minimum size of an aliquot that is representative for the whole bottle. As long as this minimum sample size is respected, within-bottle inhomogeneity does not influence the uncertainty of the certified values. Quantification of within-bottle inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-bottle homogeneity

The between-bottle homogeneity was evaluated to ensure that the certified values of the CRM are valid for all bottles of the material, within the stated uncertainty.

The number of selected bottles corresponds to approximately the cubic root of the total number of the produced bottles. 20 bottles were selected using a random stratified sampling scheme covering the whole batch for the between-bottle homogeneity test. For this, the batch was divided into 20 groups (with a similar number of bottles) and one bottle was selected randomly from each group. Three independent samples were taken from each selected bottle, and analysed by DMA for Hg (sample intake 62 mg) or EDXRF for all other elements (discs prepared from the granulate). The measurements were performed under repeatability conditions and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results are shown as graphs in Annex A. Note that the results were obtained by one laboratory only. Although the absolute values of several elements differ from the certified values, this should not influence the homogeneity assessment, which compares only results within the measurement series.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence or the analytical sequence were detected.

All datasets were tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the bottle means. Some outlying individual results, but no outlying bottle means, were detected. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Quantification of between-bottle inhomogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-bottle variation (s_{bb}) from the within-bottle variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole bottle.

Evaluation by ANOVA requires bottle means which follow at least a unimodal distribution and results for each bottle that follow unimodal distributions with approximately the same standard deviations. Distribution of the bottle means was visually tested using histograms and normal probability plots. Too few data are available for each bottle to make a clear statement of the distribution of the individual data for each bottle. Therefore, it was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-bottle standard deviations. The results of all statistical evaluations are given in Table 2.

Table 2: Results of the statistical evaluation of the homogeneity studies. Outliers were tested at a 99 % confidence level, trends were tested on a 95 % confidence level.

Element	Trends (before correction)		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Bottle means	Individual results	Bottle means
As	no	no	none	none	normal	normal
Br	no	no	1 - retained	none	normal	normal
Cd	no	no	none	none	normal	normal
Cl	no	no	none	none	normal	normal
Cr	no	no	1 - retained	none	unimodal	normal
Hg	no	no	none	none	normal	normal
Pb	no	no	none	none	normal	normal
S	no	no	none	none	normal	normal
Sb	no	no	none	none	normal	normal
Sn	no	no	none	none	normal	normal
Zn	no	no	1 - retained	none	normal	normal

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-bottle variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [10]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–bottle standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \qquad \textbf{Equation 1}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \qquad \textbf{Equation 2}$$

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}} \qquad \textbf{Equation 3}$$

MS_{within} mean square within a bottle from an ANOVA

$MS_{between}$ mean squares between-bottle from an ANOVA

$\bar{y}$ mean of all results of the homogeneity study

n number of replicates per bottle

$v_{MSwithin}$ degrees of freedom of MS_{within}

The results of the evaluation of the between-bottle variation are summarised in Table 3. The resulting values from the above equations were converted into relative uncertainties. In most cases, the uncertainty contribution for homogeneity was below 1 %. The only notable exceptions are Cr, Cl, Hg and S, where significant inhomogeneities were found. However, the results for the between-bottle variation for these elements were confirmed using the data from the short-term stability study, which comprised the same number of bottles and replicates.

Table 3: Results of the homogeneity study

Element	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
As	3.17	n.c.	0.86	0.86
Br	1.23	0.42	0.34	0.42
Cd	2.98	n.c.	0.81	0.81
Cl	14.69	4.88	4.01	4.88
Cr	4.90	1.59	1.34	1.59
Hg	3.28	1.87	0.90	1.87
Pb	1.46	n.c.	0.40	0.40
S	10.50	3.91	2.87	3.91
Sb	3.51	0.71	0.96	0.96
Sn	3.28	n.c.	0.89	0.89
Zn	1.08	0.64	0.29	0.64

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

The homogeneity study showed no outlying bottle means or trends in the filling sequence. Therefore the between-bottle standard deviation can be used as an estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution of homogeneity to account for potential inhomogeneity.

4.2 Within-bottle homogeneity and minimum sample intake

The within-bottle homogeneity is closely correlated to the minimum sample intake. Individual aliquots of a material will not contain exactly the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole bottle and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

The minimum sample intake of the material was determined using solid sampling ICP-AES in the same way as has been described for solid sampling ETAAS [11] for As, Br, Cd, Cr, Hg, Pb, S, Sb, Sn and Zn.

Samples were cut using a ZrO_2 cutting tool and analysed on an ARCOS EOP ICP-spectrometer (SPECTRO A. I. GmbH & Co. KG, Kleve, Germany) in axial (EOP) observation of the ICP plasma equipped with a electrothermal vaporization unit (ETV 4050 A, Spectral Systems, Fürstenfeldbruck, Germany).

Sample intakes of about 0.3-0.5 mg were used. 17 individual pieces were measured and two subsamples were taken from each piece. The dataset for Cr contained two large outliers being 4 and 5 times higher than the other results. These might have been caused by the use of a stainless steel needle for picking up the samples and transferring them into the vaporisation unit. As all pigments were milled together, any "nugget" would be expected to contain more than one pigment, causing high values for several elements, but this was not seen for the other elements in the same vaporisations.

Inclusion of the outliers for Cr would result in a minimum sample intake of 1200 mg to achieve a repeatability of 1.2 %. This is contradicted by the results obtained by laboratory 5d,

which obtained a relative standard deviation of 1.6 % for Cr on a sample intake of 150 mg. Also the repeatabilities obtained from the other laboratories on similarly low sample intakes are low, showing that these outliers do not reflect reality. It was therefore concluded that the high values were due to some unidentified analytical artefact. These two values were removed from the evaluation.

The data was evaluated according to the following equation [12]:

$$m_{\min} = \left(\frac{k_2' \cdot s_{m,rel}}{u_{\text{target, rel}}} \right)^2 \cdot \overline{m} \qquad \textbf{Equation 4}$$

with $m_{\min}$ minimum sample mass, k'_2 factor for the two-sided 95 % tolerance limits for a normal distribution, $s_{m,\text{rel}}$ relative standard deviation of the homogeneity experiment, $u_{target,rel}$ maximum relative uncertainty acceptable for subsampling and $\overline{m}$ the average mass used during the measurements (0.399 mg). Two times the uncertainty of characterisation ($u_{\text{char,rel}}$) as listed in Table 10 was used for $u_{\text{target,rel}}$. The resulting minimum sample masses are summarised in Table 4.

Table 4: Minimum sample masses for the uncertainty of characterisation as determined by solid sampling ICP-AES

Element	$s_{\text{m,rel}}$ [%]	$u_{\text{char,rel}}$ [%]	$m_{\min}$ [mg]
As	5.8	1.6	7
Br	7.3	2.2	6
Cd	11.1	1.2	44
Cr	14.7	1.2	86
Hg	12.1	2.3	16
Pb	9.0	1.2	31
S	5.6	2.8	2
Sb	8.7	1.7	14
Sn	9.1	1.5	21
Zn	6.4	1.7	8

The overall minimum sample intake for this material, valid for all elements investigated is set to 90 mg. No data are available for Cl due to the slight Cl contamination of the CF_4 used as modifier. The minimum sample intake for Cl is derived from the characterisation study: Several participants used sample intakes of 150 mg. The repeatability of the results (1.4-6.3 %) demonstrates the homogeneous distribution of Cl on that level.

5 Stability

Time, temperature and radiation were regarded as the most relevant influences on the stability of the material. The influence of ultraviolet or visible radiation is minimised by the choice of the containment (amber glass bottles) which eliminates most of the incoming light. Also, materials are stored and dispatched in the dark, thus largely eliminating the possibility of degradation by radiation. Despite these precautions, stability of the samples against UV light was tested to assess any potential influence of radiation. This was also to assess the long-term stability of the material.

Stability assessment is necessary to establish conditions for storage (long-term stability) as well as for dispatch of the material to the customers (short-term stability). During transport, especially in summer time, temperatures of up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature will be applied.

The short-term stability study was carried out using an isochronous design [13]. Following this approach, samples are stored for a particular time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the samples are analysed simultaneously under repeatability conditions which significantly improves the sensitivity of the stability tests.

5.1 Short-term stability study

For the short-term stability study at elevated temperature, samples were stored at 60 °C for 0, 1, 2 and 4 weeks. The reference temperature was set to -20 °C. Five bottles per storage time were selected using a random stratified sampling scheme. From each bottle, three independent subsamples were measured by DMA (Hg) or EDXRF (all other elements). The measurements were performed under repeatability conditions and in a randomised sequence to be able to separate a potential analytical drift from a trend over storage time.

The results were screened for outliers using the single and double Grubbs test. In total two outliers (one in the dataset for Cl, one in the dataset for Pb) were detected. (Table 5). As no technical reason for the outliers could be found all data were retained for statistical analysis.

Furthermore, the data were evaluated against storage time and regression lines of mass fraction versus time were calculated. The slopes of the regression lines were tested for statistical significance (loss/increase due to shipping conditions). None of the slopes of the regression lines was significantly different from zero (on 99 % confidence level) at 60 °C. Tentative removal of the two outliers did not change this assessment, demonstrating that the outliers did not mask a potential slope.

For testing the influence of UV irradiation, the granulate was placed in a single layer under an UV lamp (Sylvania G, 8W; distance from the lamp about 1 cm) and irradiated for 178 h. This intensive irradiation led to a slight colour change of the material (see Figure 3). Irradiated and non-irradiated samples were then analysed in one analytical run by digestion-ICP-AES. No significant difference between the element mass fractions in irradiated and non-irradiated samples was found (data not shown). Also the temperature/pressure profile as measured by the microwave digestion system did not differ significantly between irradiated and non-irradiated samples, demonstrating also the structural stability of the polymer matrix against long-term exposure to UV radiation.

Figure 3: ERM-EC680m after 178 h of UV irradiation. Left: irradiated sample; right: non-irradiated sample

The results of the measurements are shown in Annex B. The results of the statistical evaluation of the short-term stability are summarised in Table 5.

Table 5: Results of the short-term stability tests. Outliers and trends were tested on a 99 % confidence level.

Element	Number of individual outlying results	Significance of the trend
As	none	no
Br	none	no
Cd	none	no
Cl	1 (retained)	no
Cr	none	no
Hg	none	no
Pb	1 (retained)	no
S	none	no
Sb	none	no
Sn	none	no
Zn	none	no

The fact that neither temperature nor UV irradiation influenced the element mass fractions demonstrates that the material can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability

Stability during storage was assessed using data from the two previous batches of trace metals in plastic, based on the following considerations:

- Polyethylene is a very stable material. No plasticisers were added to prevent a change of mass by desorption of volatile compounds.
- Most pigments used are inorganic and are protected from environmental influences by the LDPE matrix and the amber glass bottle.
- All pigments (including the organic ones) used for ERM-EC680m, except SnS_2, Pb_3O_4, $CaCrO_4$ were also used in the production of ERM-EC680k and ERM-EC681k. This means that stability data on these previous batches give information on the stability of these pigments in a polyethylene matrix.
- Photo-oxidation of CdS to sulfates, carbonates and oxalates has been reported for paintings [14], but only over time scales of several decades.
- Pb_3O_4 is insoluble in water and alcohol, but soluble in hydrochloric and nitric acid and it also decomposes at temperatures above 500 °C. However, none of these conditions are expected in the storage of the CRMs. The stability of the pigment under normal storage conditions is shown by the still bright colours of medieval manuscripts that often used it [15].
  SnS_2 is also a pigment with a long history of use: it has been used under the name "Mosaic gold" and its production is described as early as in the 15th century. Its use in several 14th and 15th century manuscripts demonstrates its stability under careful storage conditions [16]. The material is insoluble in water, but soluble in aqua regia and in alkaline solutions. It decomposes at 600 °C [17], showing its thermal stability.
  $CaCrO_4$ is soluble in water and acids, but is, like the other pigments, protected by the polyethylene matrix. It is a relatively recent pigment, which was first produced in the 19th century [16]. It is used as a pigment and as a corrosion inhibitor.
  This means that historical evidence is available for the stability of Pb_3O_4 and SnS_2. Based on its chemical properties, also $CaCrO_4$ should be stable, as long as the pigment itself is not brought into contact with water or reducing substances. As LDPE has a very low permeability to water, significant dissolution is virtually impossible and any actual effect will be picked up by the stability monitoring of the material conducted by IRMM.
- The first materials, ERM-EC680 and ERM-EC681 were produced in 1999. Stability tests in 2005 showed no degradation. The material was also used as quality control material in the certification of ERM-EC680k and ERM-EC681k and the mean of laboratory mean element mass fractions obtained on the materials at that time agreed with the certified values for all elements except Cr and Br at the low level, where differences of 4.4 % (Br) and 3.1 % (Cr), respectively, were observed.
- The follow-up batches ERM-EC680k and ERM-EC681k were produced in October 2006. Stability was confirmed by the stability monitoring performed in 2013, although there was disagreement between the two laboratories performing the test on the As mass fraction: one laboratory found a lower value, whereas the result of the other laboratory agreed with the certified value. Samples of this material were also used as quality control samples in the characterisation study of ERM-EC680m and ERM-EC681m and the mean of laboratory means agreed within the respective uncertainties with the certified values for all elements except As.
- The data from the characterisation of ERM-EC680k, the stability test in 2013 and the combined result of the technically accepted data obtained (see section 6.4.1) during the characterisation study of ERM-EC680m are shown in Table 6. All data agreed within the respective uncertainties with the certified values except the mean value for As obtained during the characterisation study for ERM-EC680m. A potential explanation for this effect could be the conversion of As_2O_3 to volatile AsH_3 by the hydrogen available in the polymer. Nevertheless, the stability data from the stability test in 2013 also confirm

stability for As for at least seven years. This confirms the stability of the material for all elements except As, which seems to change over time.

Table 6: Data available for the stability of ERM-EC680k: Certified values for ERM-EC680k and their standard uncertainty obtained in October 2006 (Sn and Zn are indicative values only), stability monitoring data and their uncertainties obtained in 2013 and mean of laboratory means and its standard error obtained in the characterisation study of ERM-EC680m in September 2015. For Cr and Sn (2015 data), only the data from k_0NAA were used, as ERM-EC680k contains pigments that are only partially acid-digestible.

Element	Characterisation study 2006: certified value ± u	Stability monitoring: average ± s (n=6)	Characterisation study 2015: average of the QC sample ± se
As	4.10 ± 0.25	4.55 ± 0.24* 3.49 ± 0.78	3.18 ± 0.15
Br	96 ± 2	103.1 ± 0.6	94.3 ± 2.3
Cd	19.6 ± 0.7	21.4 ± 0.5	19.63 ± 0.19
Cl	102.2 ± 1.5	100 ± 2	105.9 ± 2.3
Cr	20.2 ± 0.4	19.7 ± 0.3	19.90 ± 0.28
Hg	4.64 ± 0.1	4.84 ± 0.15	4.53 ± 0.09
Pb	13.6 ± 0.3	13.3 ± 0.2	13.70 ± 0.19
S	76 ± 2	71 ± 2	71.2 ± 2.0
Sb	10.1 ± 0.8	9.94 ± 0.10	9.8 ± 0.2
Sn	15.3 ± 1.4	not determined	18.0 ± 0.6
Zn	137 ± 10	not determined	137.8 ± 1.8

* For As, the results of the two laboratories performing the stability test 2013 are given.

The data of the short-term stability study that demonstrated stability both at elevated temperatures as well as against UV irradiation shows that the stability of ERM-EC680m is as good as the stability of ERM-EC680k. Therefore, the stability of ERM-EC680m can be assessed using the data available for ERM-EC680k.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during dispatch were estimated as described in [18] for each element. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution u_{sts} is calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{tt} \qquad \textbf{Equation 5}$$

RSD relative standard deviation of all results of the stability study

x_i result at time point *i*

$\bar{x}$ mean results for all time points

t_{tt} chosen transport time (1 week at 60 ºC)

Uncertainties of stability during storage were estimated using the long-term stability data available for ERM-EC680k estimated using an approach equivalent to the one for the short-term stability, but adapted to only two time points: The standard uncertainties of the characterisation study 2006 and of the results of the longest time that confirmed stability (stability test 2013 for As; characterisation study 2015 for all other elements) were combined. This combined uncertainty reflects the uncertainty of stability during the period covered (7 years for As; 9 years for all other elements). The uncertainty of stability for a shelf life of 3 years was therefore estimated as

$$u_{lts,rel} = \frac{\sqrt{u_{1,rel}^2 + u_{2,rel}^2}}{t_{study}} \cdot t_{sl}$$ **Equation 6**

$u_{1,rel}$, $u_{2,rel}$ uncertainties at the two time points used for the long-term assessment

t_{sl} chosen shelf life (36 months at 18 ºC)

t_{study} time difference between the time-points used for the long-term assessment (7 years for As; 9 years for all other elements)

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies. The uncertainty describes the possible change during a dispatch at 60 °C lasting for one week.
- $u_{lts,rel}$, the stability during storage. This uncertainty contribution was estimated from the data obtained on ERM-EC680k. The uncertainty contribution describes the possible degradation during 3 years (or 36 months) storage at 18 °C.

The results of these evaluations are summarised in Table 7.

Table 7: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 3 years

Element	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
As	0.31	2.81
Br	0.14	1.06
Cd	0.29	1.24
Cl	1.26	0.91
Cr	0.49	0.80
Hg	0.39	0.98
Pb	0.43	0.76
S	1.07	1.25
Sb	0.33	2.72
Sn	0.36	3.34
Zn	0.13	2.47

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to assess its further stability. Special emphasis will be put on As, for which there is indication of a change over time.

6 Characterisation

The material characterisation is the process of determining the assigned property values of a reference material.

The material characterisation was based on an interlaboratory comparison of expert laboratories, i.e. the element mass fractions of the material were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

Twelve laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices as demonstrated by good performance in past characterisation studies organised by JRC-IRMM. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where the scope of accreditation covers the measurements, the accreditation number is stated in the list of participants (Section 0).

6.2 Study setup

Laboratories could apply more than one method for each element, resulting in several datasets for these laboratories. For each dataset, each laboratory received two bottles of ERM-EC680m and was requested to provide six independent results, three per bottle.

The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if necessary) and measurements had to be spread over at least two days to ensure intermediate precision conditions. An independent calibration was performed for each result.

Each participant received samples of ERM-EC680k as a quality control material (QCM). The results for this sample were used to support the evaluation of the characterisation results. This material contains Cr and Sn species that are not acid digestible, which means the results on these materials are not suitable for checking laboratory bias for these elements. As mentioned above, the average of As also differed from the certified value. Deviations for As for all methods are therefore expected and were not used for assessment of a method bias.

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 Methods used

A variety of digestion methods (different equipment, different acid mixtures, pressure/temperature programs; combustion in oxygen) with different quantification steps (ICP-QMS, ICP-SFMS, ICP-AES, ETAAS, CV-AAS, CV-AFS, combustion-IC, combustion-IR) as well as a method that does not need digestion (k_0NAA) were used. The combination of results from methods based on entirely different principles mitigates undetected method bias.

All methods used during the characterisation study are summarised in Annex C. The laboratory-method code consists of a number assigned to each laboratory (e.g. L01), a letter (in case the laboratory provided more than one dataset) and abbreviation of the measurement method used, (e.g. ICP-AES). The laboratory number (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 0.

6.4 Evaluation of results

The characterisation campaign resulted in 7-18 datasets per element. All individual results of the participants, grouped per element are displayed in tabular and/or graphical form in Annex D. Several datasets coming from the same laboratory were treated as independent, even if in some cases the same digestion technique was used. The fact that the digestion technique is often the same does not significantly compromise the independence of results – the potential digestion techniques are limited and no significant laboratory bias was visible for these data.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested measurement protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the measurement protocol: sample preparations and measurements performed on two days; each result for each element obtained from a separate sample preparation;
- the absence of values given as below limit of detection or below limit of quantification;
- method performance, i.e. agreement of the measurement results with the assigned value of the QC sample.

During the investigation of data, the following technical issues were noticed:

L1a: Results obtained by ICP-QMS on the QCM are consistently 10-20 % below the results from other laboratories, indicating a procedure bias for this method. Furthermore, the laboratory used pure nitric acid without addition of HF or HCl, which leads to losses for Hg, and maybe also for Sb and Sn due to formation of hydrolysis products. Finally, the laboratory reported uncertainties of 40 % for all elements. These uncertainties are too high for characterisation of a CRM and the data were not used for the value assignment.
L1b: The laboratory reported uncertainties of 40 % for all elements. These uncertainties are too high for characterisation of a CRM and the data were not used for the value assignment.

L2a: The results for Pb for the two CRMs that were used as QCMs deviated from the certified value, indicating a method bias. The data were therefore not used for value assignment.
L2d: The laboratory reported an expanded uncertainty of 50 % for Cl which is too high for characterisation of a CRM. The data were not used for the value assignment.

L5a: The laboratory reported biased results for Cr in the QCM. It re-checked the concentration of the spike for Cr by reverse-IDMS using two independent calibration solutions (multi II A Spex and Merck VI) and found that the content on the certificate was biased by a factor 1.2 and the results were corrected for this bias. However, as this investigation was performed as a reaction to a disclosure of results, the data were not used for the value assignment.
L5a, c, d: The laboratory reported very high uncertainties for Sn and Cr. These high uncertainties are due to the high uncertainty of trueness which was obtained by the bias seen from the analysis of ERM-EC680k and ERM-EC681k. This bias is caused by the presence of insoluble pigments in ERM-EC680k and ERM-EC681k. As the candidate material ERM-EC680m does not contain acid insoluble pigments, these uncertainties are therefore overestimated. The results for Sn and Cr are therefore retained.
L5b: The results obtained by AFS for for Hg for the two CRMs used as QCM differed from the certified values. The values of AFS for Hg were therefore not used for characterisation.

L5f: The results obtained for S by combustion-IR on the low-level CRM used as QCM (ERM-EC680k) differed from the certified value. The results were not used for characterisation.

L6a: The result for Hg on the CRMs used as QCMs obtained by ICP-IDMS differs from the certified values. The result was therefore not used for value assignment.

L6c: The laboratory used ICP-MS for the determination of Cl, which in itself is unusual due to the low ionisation yield for this element. The laboratory also stated itself not to have a lot of experience in the determination of Cl, which is reflected in the rather low uncertainty stated (8 %). This, together with the fact that the result on the QCM used for the characterisation of ERM-EC681m was biased casts doubts on the validity of the method for the deterjmination of Cl. The data were therefore not used for value assignment.

L7a: The result for Hg on the CRMs used as QCMs obtained by ICP-IDMS differs from the certified values. After replacement some parts, amongst them the detector, the solutions were re-measured and the results for the QCMs agreed with the certified values. However, the results of the new measurements were not used for value assignment as these measurements were performed only after disclosure of the results from the other laboratories.

L8a: The data for As for the QCM shows a large variation between the two measurement days. Although this difference was not visible in the candidate CRM, the data were not used for characterisation. The data for Cd showed a huge variation between the two measurement days. The laboratory stated that this variation is higher than what they normally observe in the laboratory, indicating method problems. The data were therefore not used for characterisation.

The uncertainty stated for Sn (46 %) is too high for characterisation of a CRM. The result was therefore not used for value assignment.

L9: The laboratory used pure nitric acid for digestion, which may lead losses of Sn and Sb due to the formation of oxydhydrates. The high standard deviations of results on ERM-EC680m for Sn supports this suspicion. The data for Sn and Sb were therefore not used for characterisation, even if they agreed with the certified values.

Four results for As were below the limit of detection, showing that data are close to the limit of detection and far below the limit of quantification. The data were therefore not used for characterisation.

The results for Cd and Pb obtained on the CRMs used as QCMs differ from the certified values, indicating method bias. The results were not used for characterisation.

The issues and actions taken are summarised in Table 8.

Table 8: Summary of the technical noteworthy issues and actions taken in response to them

Element	Lab-method code	Description of issue	Action taken
As	L1a-ICP-QMS	Procedure bias; too high uncertainties	Data not used for evaluation
	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L8a-ETAAS	Data for the QCMs show a huge difference between day 1 and day 2	Data not used for evaluation
	L9-ICP-AES	4 results for ERM-EC680m are given as < LOD, showing that the method is not sensitive enough	Data not used for evaluation

Element	Lab-method code	Description of issue	Action taken
Cd	L1a-ICP-MS	Procedure bias; too high uncertainties	Data not used for evaluation
	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L8a-ETAAS	Data measured on day 1 and 2 differ by 40 %	Data not used for evaluation
	L9-ICP-AES	Result for the QCM differs from the certified value	Data not used for evaluation
Cl	L2d-comb-IC	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L6c-ICP-SFMS	Method no very suitable for Cl; bias on the QCM of a simultaneous characterisation study	Data not used for evaluation
Cr	L1a-ICP-MS	Procedure bias; too high uncertainties	Data not used for evaluation
	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L5a-ICP-IDMS	Spike was found biased.	Data not used
	L5c-ICP-MS, L5d-ICP-AES	Uncertainty is very high (80 %), but this is due to the inclusion of the bias determined on ERM-EC680k, which contains non-digestible Cr_2O_3.	Data retained
Hg	L1a-ICP-MS	Procedure bias; use of pure HNO_3 for digestion; too high uncertainties	Data not used for evaluation
	L5b-AFS	Result for both QCMs differ from certified value	Data not used for evaluation
	L6a-ICP-IDMS	Result for the QCM differs from certified value	Data not used for evaluation
	L7a-ICP-IDMS	Result for the QCM differs from certified value	Data not used for evaluation
Pb	L1a-ICP-MS	Procedure bias; too high uncertainties	Data not used for evaluation
	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L2a-AAS	Result for the QCM deviates from certified value	Data not used for evaluation
	L9-ICP-AES	Result for the QCM differs from the certified value; reproducibility is rather poor (presumably due to the high dilution)	Data not used for evaluation
S	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation
	L5f-Comb-IR	Result for the QCM differs from the certified value.	Data not used for evaluation

Element	Lab-method code	Description of issue	Action taken
Sb	L1a-ICP-MS	Procedure bias; use of pure HNO_3 for digestion; too high uncertainties	Data not used for evaluation
	L9-ICP-AES	Use of pure HNO_3 for digestion	Data not used for evaluation
Sn	L1a-ICP-MS	Procedure bias; use of pure HNO_3 for digestion; too high uncertainties	Data not used for evaluation
	L5d-ICP-SFMS	Uncertainty is very high (80 %), but this is due to the inclusion of the bias determined on ERM-EC680k, which contains non-digestible SnO_2.	Data retained
	L8a-ETAAS	Uncertainty is too high for the characterisation of a CRM	Data not used for evaluation
	L9-ICP-AES	Use of pure HNO_3 for digestion	Data not used for evaluation
Zn	L1a-ICP-MS	Procedure bias; too high uncertainties	Data not used for evaluation
	L1b-ICP-AES	Uncertainty is too high for characterisation of a CRM	Data not used for evaluation

6.4.2 Statistical evaluation

The technically accepted datasets were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots. They were also analysed outlying means using the Grubbs test and for outlying standard deviations using the Cochran test, (both at a 99 % confidence level). Standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 9.

Table 9: Statistical evaluation of the technically accepted datasets. *p*: number of technically valid datasets

Element	*p*	Outliers		Normally distrib.?	Statistical parameters			
		Means	Variances		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
As	12	none	none	approx.	4.666	0.257	0.244	0.195
Br	7	none	none	yes	180.5	10.6	10.3	5.7
Cd	15	none	none	yes	20.75	1.00	0.95	0.74
Cl	5	none	none	yes	84.25	7.54	7.36	3.96
Cr	16	none	L5c, L8a (retained)	yes	9.610	0.448	0.393	0.529
Hg	8	none	none	yes	2.563	0.164	0.159	0.093
Pb	12	none	none	yes	11.33	0.46	0.41	0.50
S	6	none	L6b (retained)	approx.	86.06	5.97	5.87	2.75
Sb	13	none	L8a (retained)	yes	9.588	0.590	0.550	0.528
Sn	12	L11 (retained)	L3, L10 (retained)	not normal	20.68	1.04	0.92	1.18
Zn	16	none	L8a (retained)	approx.	193.8	12.9	12.6	6.6

The datasets for As, Br, Cd, Cl, Cr, Hg, Pb, S, Sb and Zn do not contain outlying mean values and the data follow normal, or approximately normal distributions. The statistical evaluation flagged some data as outliers of variance. This merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value.

The statistical evaluation flagged laboratory L11 as an outlier for measurand Sn, which also causes the distribution deviate from normality. However, it must be borne in mind that outlier tests do not take uncertainty information into consideration. A closer investigation reveals that the difference between the mean value of laboratory L11 and the other results is covered by the measurement uncertainty of laboratory L11. There is therefore no evidence that the results of laboratory L11 deviate from the other results. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value.

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table 10).

Table 10: Uncertainty of characterisation for ERM-EC680m

Element	*p*	Mean [mg/kg]	*s* [mg/kg]	$u_{char,rel}$ [%]
As	12	4.666	0.257	1.59
Br	7	180.5	10.6	2.22
Cd	15	20.75	1.00	1.24
Cl	5	84.25	7.54	4.00
Cr	16	9.610	0.448	1.17
Hg	8	2.563	0.164	2.26
Pb	12	11.33	0.46	1.17
S	6	86.06	5.97	2.85
Sb	13	9.588	0.590	1.71
Sn	12	20.68	1.04	1.45
Zn	16	193.8	12.9	1.66

7 Value Assignment

Certified and indicative values were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM generally require pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets following the 'Guide to the Expression of Uncertainty in Measurement' [3] were established

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. Uncertainties are evaluated according to the same rules as for certified values.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 9 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during

transport (u_{sts}) and long-term storage, u_{lts} (Section 0). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM, rel}$) with a coverage factor *k* as:

$$U_{CRM,rel} = k \cdot \sqrt{u^2_{char,rel} + u^2_{bb,rel} + u^2_{sts,rel} + u^2_{lts,rel}}$$ **Equation 7**

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1
- u_{sts} was estimated as described in section 5.3
- u_{lts} was estimated as described in Section 5.3.

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor *k* of 2 was applied, to obtain the expanded uncertainties

The certified values and their uncertainties are summarised in Table 11.

Table 11: Certified values and their uncertainties for ERM-EC680m

Element	Certified value[1)] [mg/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [1)]
As	4.7	1.59	0.86	0.31	3.35	6.71	0.4
Br	181	2.22	0.42	0.14	2.50	4.99	9
Cd	20.8	1.24	0.81	0.29	1.96	3.92	0.9
Cr	9.6	1.17	1.59	0.49	2.18	4.36	0.5
Hg	2.56	2.26	1.87	0.39	3.12	6.24	0.16
Pb	11.3	1.17	0.40	0.43	1.52	3.03	0.4
S	86	2.85	3.91	1.07	5.10	10.20	9
Sb	9.6	1.71	0.96	0.33	3.37	6.74	0.7
Sn	20.7	1.45	0.89	0.36	3.76	7.53	1.6
Zn	194	1.66	0.64	0.13	3.05	6.10	12

[1)] Expanded (*k* = 2) and rounded uncertainty.

7.2 Indicative values and their uncertainties

Indicative values were assigned for Cl as only five valid datasets are available for characterisation. The uncertainty budgets were set up as for the certified values and are listed together with the assigned values in Table 12.

Table 12: Indicative value and its uncertainty for ERM-EC680m

Element	Indicative value[1)] [mg/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [1)]
Cl	84	4.00	4.88	1.26	8.85	13.00	11

[1)] Expanded (*k* = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

All elements are chemically well-defined substances. The participants used different methods for the sample preparation as well as for the final determination, demonstrating the absence of measurement bias. The measurand is therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. Different calibrants and specified traceability of their assigned values were used and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as it is also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific (or specific groups) of analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CLSI Guideline C-53A [19] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

ERM-EC680m was produced from commercial polymers and commercially available pigments. The analytical behaviour will be the same as for a routine sample of coloured polyethylene. For samples other than polyethylene the commutability has to be assessed.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials shall be stored at (18 ± 5) °C in the dark. The user is reminded to close bottles immediately after taking a sample.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.3 Minimum sample intake

The minimum sample intake representative for all parameters is 150 mg for Cl and 90 mg for all other elements.

9.4 Use of the certified value

The main purpose of this material is to assess method performance, i.e. for checking the accuracy of analytical results/calibration. Note that if the tested material contains insoluble pigments, results obtained on this CRM may not be representative for the tested sample for wet digestion methods.
As any reference material, it can also be used for control charts or validation studies or calibration.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [20]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty (u_{Δ}) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as inhomogeneity was included in the uncertainties of the certified values.

Use as a calibrant

It is not recommended to use this matrix material as calibrant, because the certified values have higher uncertainties than pure standards.. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

10 Acknowledgments

The authors would like to acknowledge the support received from John Segher and Jean Charoud-Got and their team from IRMM related to the processing of this CRM and from Maria Contreras concerning the set-up of the required isochronous studies.

Also, the authors would like to thank Reinhard Zeleny and Fran Van Heuverswyn (IRMM) for reviewing the certification report, as well as the experts of the Certification Advisory Panel "CAP Element", Steve Balsley (IAEA, AT), Thomas Meisel (Montanuniversität Leoben, AT) and Peter Vermaercke (SCK-CEN, BE) for their constructive comments.

11 References

1 ISO Guide 34, General requirements for the competence of reference materials producers, International Organization for Standardization, Geneva, Switzerland, 2009

2 ISO Guide 35, Reference materials – General and statistical principles for certification, International Organization for Standardization, Geneva, Switzerland, 2006

3 ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement, (GUM 1995), International Organization for Standardization, Geneva, Switzerland, 2008

4 European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging waste

5 Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment

6 Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles

7 2005/673/EC: Council Decision of 20 September 2005 amending Annex II of Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles

8 J. Pauwels, A. Lamberty, P. De Bièvre, K.-H. Grobecker, C. Bauspiess (1994) Certified reference materials for the determination of cadmium in polyethylene, Fres. J. Anal. Chem 349: 409-411

9 A. Lamberty, W. Van Borm, Ph. Quevauviller (2001) The certification of mass fraction of As, Br, Cd, Cl, Cr, Hg, Pb and S in two polyethylene CRMs ERM-EC680 and -EC681, EUR 19450EN, ISBN 92-894-0874-X, Luxembourg, 2001

10 T.P.J. Linsinger, J. Pauwels, A.M.H. van der Veen, H. Schimmel, A. Lamberty, Homogeneity and stability of reference materials, Accred. Qual. Assur. 6 (2001) 20-25

11 M. Rossbach, K. H. Grobecker, Homogeneity studies of reference materials by solid sampling – AAS and INAA, Accred. Qual. Assur. 4 (1999) 498-503

12 J. Pauwels, C. Vandecasteele, Determination of the minimum sample mass of a solid CRM to be used in chemical analysis, Fres. J. Anal. Chem. 345 (1993) 121-123.

13 A. Lamberty, H. Schimmel, J. Pauwels, The study of the stability of reference materials by isochronous measurements, Fres. J. Anal. Chem. 360 (1998) 359-361

14 E. Pouyet, M. Cotte, B. Fayard, M. Salomé, F. Meirer, A. Mehta, E.S. Uffelman, A. Hull, F. Vanmeert, J. Kieffer, M. Burghammer, K. Janssens, F. Sette, J Mass (2015) 2D X-ray and FTIR micro-analysis of the degradation of cadmium yellow pigment in paintings of Henri Matisse, Applied Physics A (in press), doi:10./1007//s00339-015-9239-4

15 https://en.wikipedia.org/wiki/Minium_%28pigment%29; Philip Ball (2001), Bright Earth - Art and the Invention of Colour, Hazan (French edition)

16 N. Eastaugh, V. Walsh, T. Chaplin, R. Sidall: Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments, Butterworth-Heinemann, Oxford, 2008 p.82 ($CaCrO_4$); p 274 (SnS2)

17 Lide, David R., ed. (2009) CRC Handbook of Chemistry and Physics (90th ed.), Boca Raton, Florida: CRC Press. ISBN 978-1-4200-9084-0

18 T.P.J. Linsinger, J. Pauwels, A. Lamberty, H. Schimmel, A.M.H. van der Veen, L. Siekmann, Estimating the Uncertainty of Stability for Matrix CRMs, Fres. J. Anal. Chem. 370 (2001) 183-188

19 H. Vesper, H. Emons, M. Gnezda, C. P. Jain, W. G. Miller, R. Rej, G. Schumann, J. Tate, L. Thienpont, J. E. Vaks, Characterization and Qualification of Commutable Reference Materials for Laboratory Medicine; Approved Guideline, CLSI document C53-A, Clinical and Laboratory Standards Institute, Wayne, PA, USA, 2010

20 T.P.J. Linsinger, ERM Application Note 1: Comparison of a measurement result with the certified value, www.erm-crm.org (last accessed on 16.10.2015)

Annexes

Annex A: Results of the homogeneity measurements

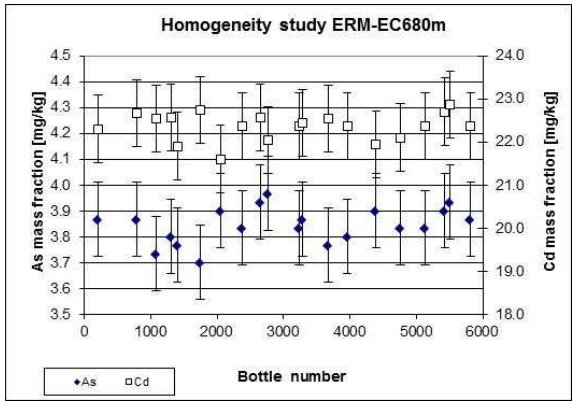
Annex B: Results of the short-term stability measurements

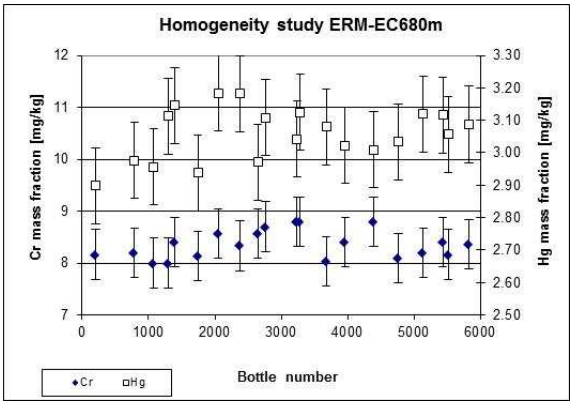
Annex C: Methods used for Characterisation

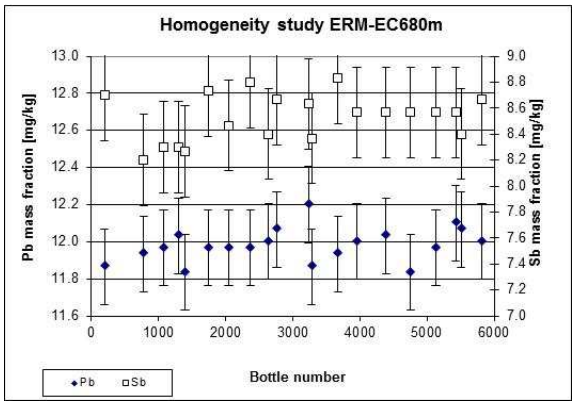
Annex D: Results of the characterisation study

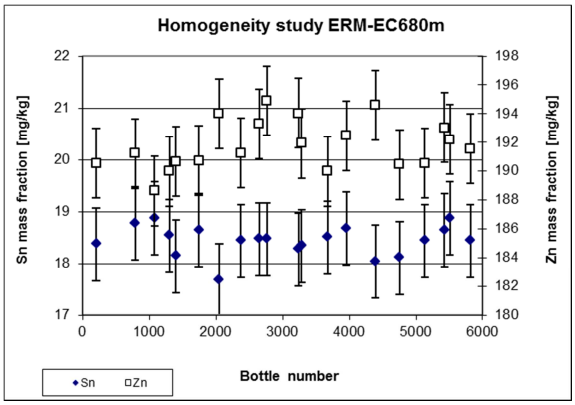
Annex A: **Results of the homogeneity study**. Shown are the bottle means and their confidence intervals (95 %; n=3), based on the within-bottle standard deviation as derived by ANOVA.

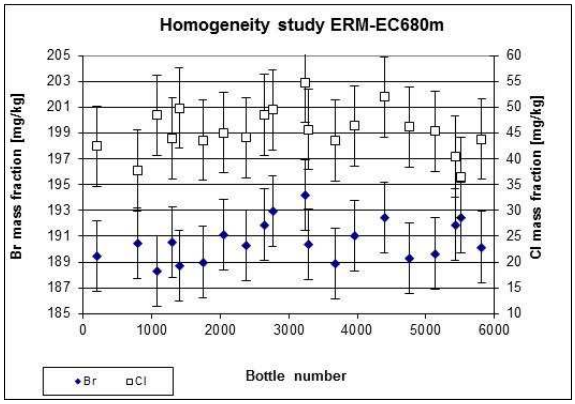
Note that the results were obtained by one laboratory only and in some cases differ from the certified value. Although the absolute values of several elements differ from the certified values, this should influence the homogeneity assessment, which compares only results within the measurement series.

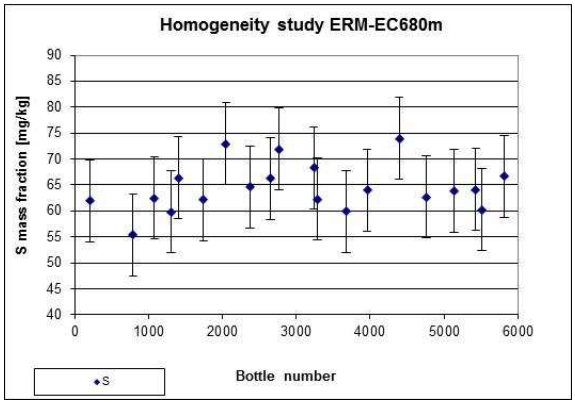






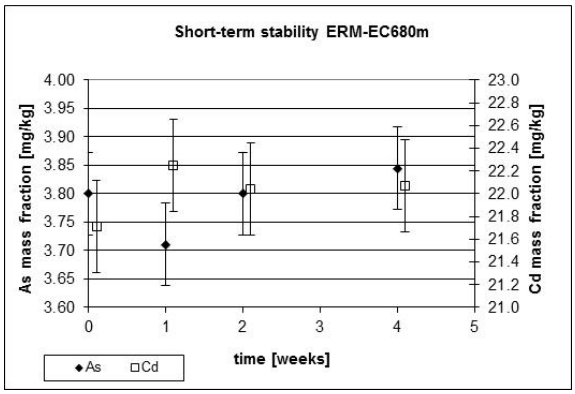


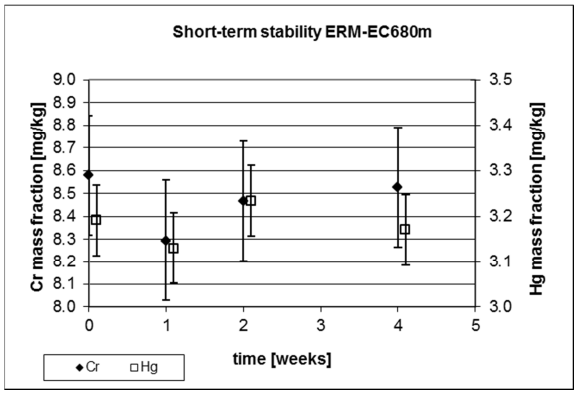


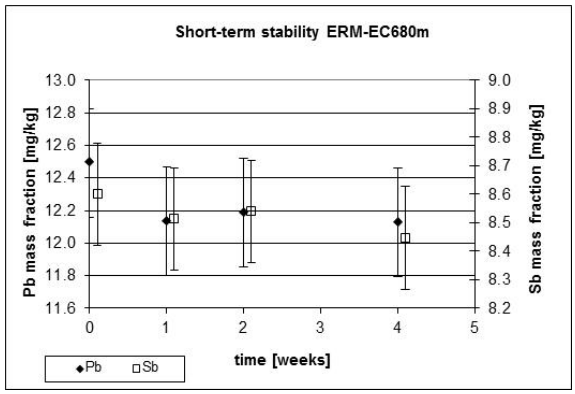


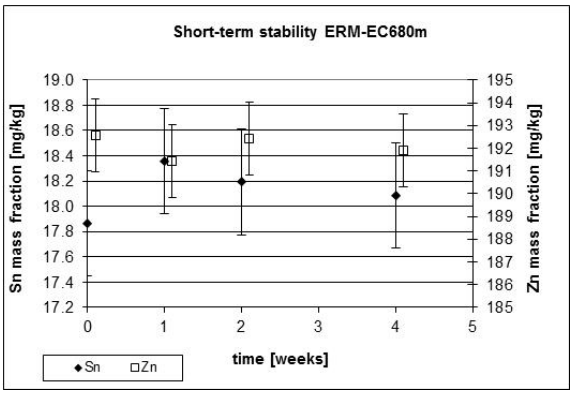
Annex B: **Results of the short-term stability study at 60 °C**. Shown are the averages per time point and their confidence interval (95 %; n=15) based on the within-group standard deviation as derived from an one-way ANOVA of all data grouped by time. The time points were 0, 1, 2 and 4 weeks for both elements in each graph, but the data were separated graphically to facilitate reading.

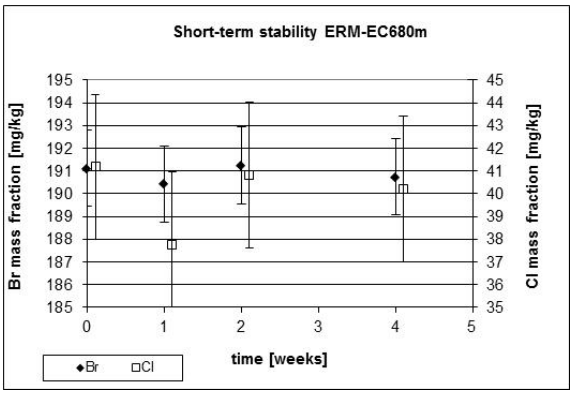
Note that the results were obtained by one laboratory only and in some cases differ from the certified value. Although the absolute values of several elements differ from the certified values, this should influence the homogeneity assessment, which compares only results within the measurement series.

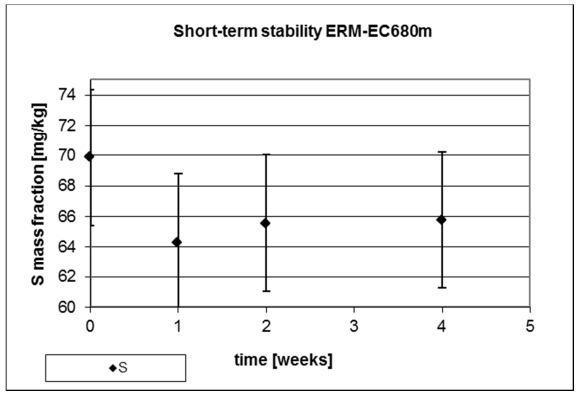












Annex C: Summary of methods used in the characterisation study.

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L1a	ICP-QMS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	200-300 mg	Closed microwave digestion using CEM Discover SP-D Explorer 24 Plus 10 mL HNO_3; 200 °C, 300 bar, 7 min Dilution to 50 mL and additional dilution 1:10	Multielement standard Romil; traceability ensured by a CRM; Internal standard: Y	ICP-MS on mass 75 (As), 111 (Cd), 52 (Cr), 202 (Hg), 208 (Pb), 121 (Sb), 118 (Sn), 66 (Zn)
L1b	ICP-AES	As, Cd, Cr, Pb, Sb	200-220 mg	Closed microwave digestion using CEM Discover SP-D Explorer 24 Plus 10 mL HNO_3; 200 °C, 300 bar, 7 min Dilution to 50 mL	Multielement standard Romil; traceability ensured by a CRM	ICP-AES on 189.042 nm (As), 228.802 nm (Cd) 267.716 nm (Cr), 220.353 nm (Pb), 182.034 nm (Sb), 206200 nm (Zn)
L2a	ETAAS CV-AAS	Cd, Pb, Sb Hg	300-500 mg	Closed microwave digestion: 1 mL HNO3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed	ETAAS according to CEN/TS 16172 (Cd, Pb, Sb) on 228.8 nm (Cd), 283.3 nm (Pb), 217.6 nm (Sb) CV-AAS according to EN ISO 12846 with reductant NaBH4 (Hg) on 253.7 nm (Hg)
L2b	ICP-QMS	As, Br, Cr, Sn, Ge, Zn	300-500 mg	Closed microwave digestion: 1 mL HNO_3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed Internal standard: Rh (As, Br), Ge (Cr, Zn), In (Sn)	ICP-MS according to EN ISO 17294-2 on mass 75 (As), 79 and 81 (Br), 52 (Cr), 118 and 120 (Sn), 68 (Zn)

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L2c	ICP-AES	S	300-500 mg	Closed microwave digestion: 1 mL HNO_3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed	ICP-OES according to EN ISO 11885 on 180.669 nm (S)
L2d	Combustion-IC	Cl	500 mg	IKA - Kalorimetersystem C 2000 basic IKA – Kalorimeterbombe C 5012 O_2, 30 bar, 30 min 10 mL aqueous absorption solution (Na_2CO_3, $NaHCO_3$, NaOH, H_2O_2)	Commercial standards	IC according to EN ISO 10304-1 (Cl)
L3	k_0NAA	As, Cd, Cr, Hg, Sb, Sn, Zn	170-200 mg	Irradiation for 1170 min at $7.4 \cdot 10^{12}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 3-6 d;	HPGe P-type, 25 % rel efficiency; measurement time 1 h
		Br, Cl,	170-200 mg	Irradiation for 1 min at $2 \cdot 10^{13}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 8 and 45 min	HPGe P-type, 25% rel efficiency; measurement time 15 and 20 min
L4	k_0NAA	As, Br, Cd, Sn	550 -700 mg	Irradiation for 15 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 2-5 d;	HPGe detector, 40 – 55 % rel efficiency; measurement time 24-48 h
		Cr, Hg, Sb, Zn		Irradiation for 420 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 15-25 d;	HPGe detector, 40 – 55 % rel efficiency; measurement time 24-48 h
		Cl		Irradiation for 15 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 30-900 s	HPGe detector, 40 – 55 % rel efficiency; measurement time 900 s

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L5a	ICP-IDMS	Cd, Cr, Pb, Zn	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Spike solution Certipur ^{111}Cd, ^{206}Pb, (Merck), enriched ^{53}Cr(VI) Applied isotope technologies), ^{68}Zn (Spex Certiprep)	Sectorfield ICP-MS on masses 11/112 (low resolution; Cd), 52/53 (medium resolution; Cr), 206/208 (low resolution; Pb), 66/68 (high resolution; Zn)
L5b	AFS	Hg	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Merck standard checked against NIST SRM 3133	AFS at 253.7 nm
L5c	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Standards from CPI international checked against NIST SRM 3100 series (As, Cd, Cr, Pb, Sn, Zn) and NIST SRM 3102a (Sb) Internal standard Rh	ICP-AES at 189.042 nm (As), 214.438 nm (Cd), 205.552 nm (Cr), 220.353 nm (Pb), 206.833 nm (Sb), 189.989 nm (Sn), 213.856 nm (Zn)
L5d	ICP-SFMS	As, Cd, Cr, Pb, Sb, Sn, Zn	150 mg	High Pressure asher 4 mL HNO_3 + 1 mL HCL at 200 °C and up to 200 bar; 210 min	Mono- and multielement standards from SPEX checked against NIST SRM 3103a (As, Cd, Cr, Pb, Zn), NIST SRM 3102a (Sb), NST SRM 3161a (Sn); internal standard Ge (As), Rh (all others)	Sectorfield ICP-MS on masses 75 (As; high resolution), 114 (Cd), 52 (Cr), 206, 207, 208 (Pb), 121 (Sb), 118 (Sn) and 66 (Zn) (all medium resolution)
L5e	Combustion/IC	Br, Cl, S	530-600 mg	Parr 6200 calorimeter 30 bar O_2, 5 mL (0.1 M NaOH solution + 3 mL H_2O_2 / L 0.1 M NaOH) in bomb and 10 mL in absorption flask	Merck standards checked against NIST NaBr in water/NaCl in water/Na2SO4 in water	IC (of 3.2 mM Na2CO3/ and 1.0 mM NaHCO3) with conductivity and UV detection in combination with conductivity suppression

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L5f	Combustion-IR	S	100-160 mg	LECO Truspec S at 3 bar aqnd 1350 C samples weighed in a dry combustion boat and covered with about 1.5 g baked white sand; combustion at 1350 °C in oxygen	LECO 502-55 (Orchard leaves), 0.148 % S	LECO Truspec S
L6a	ICP-IDMS	Cd, Cr, Hg, Pb, Zn	100-110 mg	Milestone Ultraclave at 230 °C/90 bar; 40 min ramping time, 25 min hold at 230 °C 5 ml HNO_3 / 0.020 ml HF	Isotope dilution MS characterization using enriched isotopes from Oak Ridge National Laboratory	ICP-MS on masses 111, 112, 114 (Cd), 52, 53 (Cr), 199, 200, 202 (Hg), 206, 208 (Pb), 64, 66, 67 (Zn)
L6b	ICP-SFMS	As, Cd, Cr, Hg, Pb, S, Ab, Sn, Zn	150-200 mg	Milestone Ultraclave at 230 °C for 20 min in HNO_3/HF	Standards from Inorganic Venture (Zn) and Ultra Scientific (all others); traceability via NIST 3103a (As), NIST 3108 (Cd), NIST 3112a (Cr), NIST 3133 (Hg), NIST 3128 (Pb), NIST 3154 (S), NIST 3102a (Sb), NIST 3161a (Sn), NIST 3168a (Zn) Internal standard: In	Quantification by ICP-SFMS in high resolution at mass 75 (As), medium resolution at mass 52, 53 (Cr), 32 (S), 64, 66 (Zn) and low resolution at mass 111, 114 (Cd), 201, 202 (Hg), 206, 207, 208 (Pb), 121, 123 (Sb), 118, 120 (Sn)
L6c	ICP-SFMS	Br, Cl	150-200 mg	Microwave digestion at 220 °C for 30 min in HNO_3	Standards from Ultra Scientific (Br) and Fluka (Cl); traceability via NIST 3184 (Br) and SA71387	Quantification by ICP-SFMS in medium resolution at mass 79 (Br), 35 (Cl)
L7a	ID-TIMS (Cd, Pb) ICP-IDMS (Hg)	Cd, Pb, Hg	210-240 mg	High Pressure Asher at 320 °C/130 bar for 240 min in 4.5 mL HNO_3/0.5 mL H_2O_2 Separation of the analytes by column chromatography	Double IDMS with ^{113}Cd, ^{201}Hg, ^{206}Pb, ^{207}Pb isotopic spikes from the Bundesanstalt fuer Materiaforschung und -Pruefung	Cd, Pb: Quantification by TIMS at mass 110, 111, 112, 113 and 114 (Cd) and 204, 206, 207, 208 (Pb) using a mass resolution of 400 Hg: Quantification by ICPMS at mass 201, 202 and a mass resolution of 400

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L7b	ID-TIMS	Cr	400-420 mg	Ashing in a microwave-heated muffle oven with subsequent soda fusion melting of the ash. Separation of the analytes by column chromatography	Double IDMS with ^{53}Cr from the Bundesanstalt fuer Materiaforschung und -Pruefung	Quantification by TIMS at mass 52, 53 using a mass resolution of 400
L8a	ETAAS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	200 mg	Milestone Ultraclave at 250 °C/140 bar for 30-60 min 4 mL HNO_3 + 0.2 mL $HClO_4$	Standards from ChemLal; traceability via NIST 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3133 (Hg), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NIST SRM 3168a (Zn)	ETAAS with background correction at 193.7 nm (As), 228.8 nm (Cd), 357.9 nm (Cr), 253.7 nm (Hg), 283.3 nm (Pb), 217.6 nm (Sb), 286.3 nm (Sn), 307.6 nm (Zn)
L8b	ICP-QMS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	170-180 mg	Milestone Ultraclave at 250 °C/135 bar for 45 min 4.0 mL HNO_3 + 0.1 mL HCl	Standards from inorganic Ventures with traceability via NIST SRM 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3133 (Hg), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NISt SRM 3168a (Zn) Internal standard In (mass 115)	ICP-MS at masses 75 (As), 111 (Cd), 52 (Cr), 202 (Hg), 206, 207, 208 (Pb), 121 (Sb), 118 (Sn), 66 (Zn) Mass resolution 70-280
L8c	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	200-210 mg	Milestone Ultraclave at 250 °C/140 bar for 60 min 4.0 mL HNO_3 + 0.2 mL $HClO_4$	Standards from Chemlab with traceability via NIST SRM 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NISt SRM 3168a (Zn) Internal standard Sc	ICP-AES at 188.979 nm (As), 214.438 nm (Cd), 205.56 nm (Cr), 220.353 nm (Pb), 206.836 nm (Sb), 198.933 nm (Sn), 213.856 nm (Zn)

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L9	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	200-220 mg	Microwave digestion (Milestone ETHOS 900) at 140-220 °C for 60 min 8 mL HNO_3 65%	Monoelement standards from Carlo Arba (As, Sn) multielement standards from Sigma (Cd, Cr, Pb, Sb, Zn) with traceability via NIST SRM 3103a (As), NIST SRM 728 (Cd, Pb, Zn), NIST SRM 2112 (Cr), NIST SRM 3102a (Sb)	ICP-AES at 188.979 nm (As), 226.502 nm (Cd), 267.716 nm (Cr), 220.353 nm (Pb), 206.836 nm (Sb), 189.927 nm (Sn), 206.200 nm (Zn)
L10	k0NAA	Cr, Hg, Sb, Sn, Zn As, Br, Cd, Cl	160-170 mg	Irradiation for 720 min at $1.10 \cdot 10^{12}$ neutrons/cm2/s Irradiation for 5 min at $2 \cdot 10^{13}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 19-30 d; Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 4 d (As, Br), 7-9 d (Cd), 20 min (Cl)	HPGe P-type, 40-45 % rel efficiency; measurement time 9-17 h HPGe P-type, 25% rel efficiency; measurement time 100 min (As, Br), 20 min (Cl), 9-16 h (Cd)
L11	ICP-AES	As, Cd, Cr, Pb, S, Sb, Sn, Zn	500 mg	Milestone Ultraclave at 240 °C/105 bar for 240 min 4.0 mL HNO_3 + 0.5 mL HF +0.2 mL H_2O_2	Single-element standards from Merck; traceable via NISt SRMs	ICP-AES at 189 nm & 197 nm (control) (As), 228 nm & 226 nm (control) (Cd), 267 nm & 284 nm (control) (Cr), 220 nm & 216 nm (control) (Pb), 180 nm & 182 nm (control) (S), 206 nm & 217 nm (control)(Sb), 189 nm (Sn), 213 nm & 202 nm (control) (Zn)
L12a	ICP-MS	As, Cd, Cr, Hg, Pb, S, Sb, Sn, Zn	220-250 mg	Bomb digestion (Berghof) at 220 °C/60 min 5 mL HNO_3 + 2.5 mL H_2O_2 + 0.4 mL HF (according to NEN-EN-ISO 16968)	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs	ICP-MS with collision cell technology at masses 75 (As), 111 (Cd), 52 (Cr), 201 (Hg), 208, 207, 206 (Pb), 34 (S), 121 (Sb), 118 (Sn), 66 (Zn)

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L12b	ICP-AES	As, Cd, Cr, Pb, S, Sb, Sn, Zn	250 mg	Bomb digestion (Berghof) at 190 °C/600 min 9.5g HNO_3 + 4.5 g $HClO_4$; After digestion dilution to 50 g and addition of 0.5 mL HF	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs Internal standard Sc	ICP-AES at 193.7 nm (As), 214.4 nm (Cd), 267.7 nm (Cr), 220.3 nm (Pb), 182 nm (S), 217.5 nm (Sb), 189.9 nm (Sn), 206.2 nm (Zn)
L12c	Combusion-IC	Br, Cl, S	500-700	Digestion in 30 bar oxygen (bomb calorimeter PARR 6300); bomb is rinsed with 100 mL water	Stock solutions from crystalline NaBr, NaCl and Na2SO4 (suprapur, Merck KgA, DE), checked against NIST-CRM	Ion chromatography on a Dionex IonPac AS18 (4 x 250mm) column. Gradient elution with an Eluent Generator Cartridge (KOH).
L12d	CV-AFS	Hg	250 mg	Bomb digestion (Berghof) at 190 °C/600 min 5 mL HNO_3 + 2.5 mL $HCLO_4$; After digestion dilution to 50 g and addition of 0.5 mL HF (digestion together with 12b)	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs Internal standard Sc	CV-AFS at 254 nm

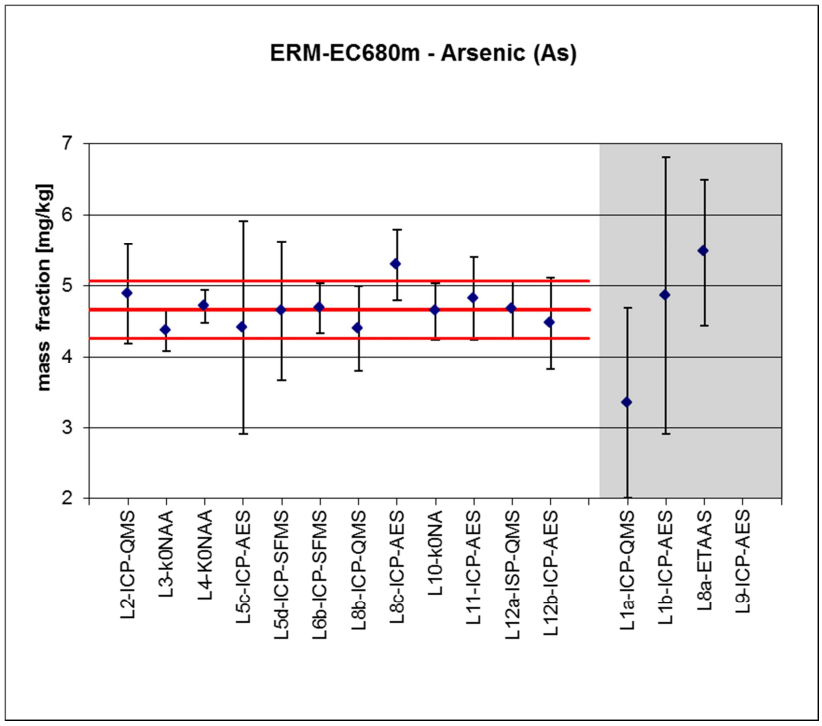
Annex D: Results of the characterisation measurements. Given are the results reported by the laboratories and the uncertainties reported for the average of 6 results (For averages marked with an asterisk, no uncertainty was given. In these cases, two times the standard deviation or the typical uncertainty obtained for other elements was entered as uncertainty.

The solid red lines in the graph (dashed for indicatice values) show the certified value and the upper and lower limit of the certified range (95 % uncertainty). Laboratories not used for value assignment are separated in the graphs by the space in these red lines.

Arsenic (results in the grey shaded part of the graph were not used for value assignment)

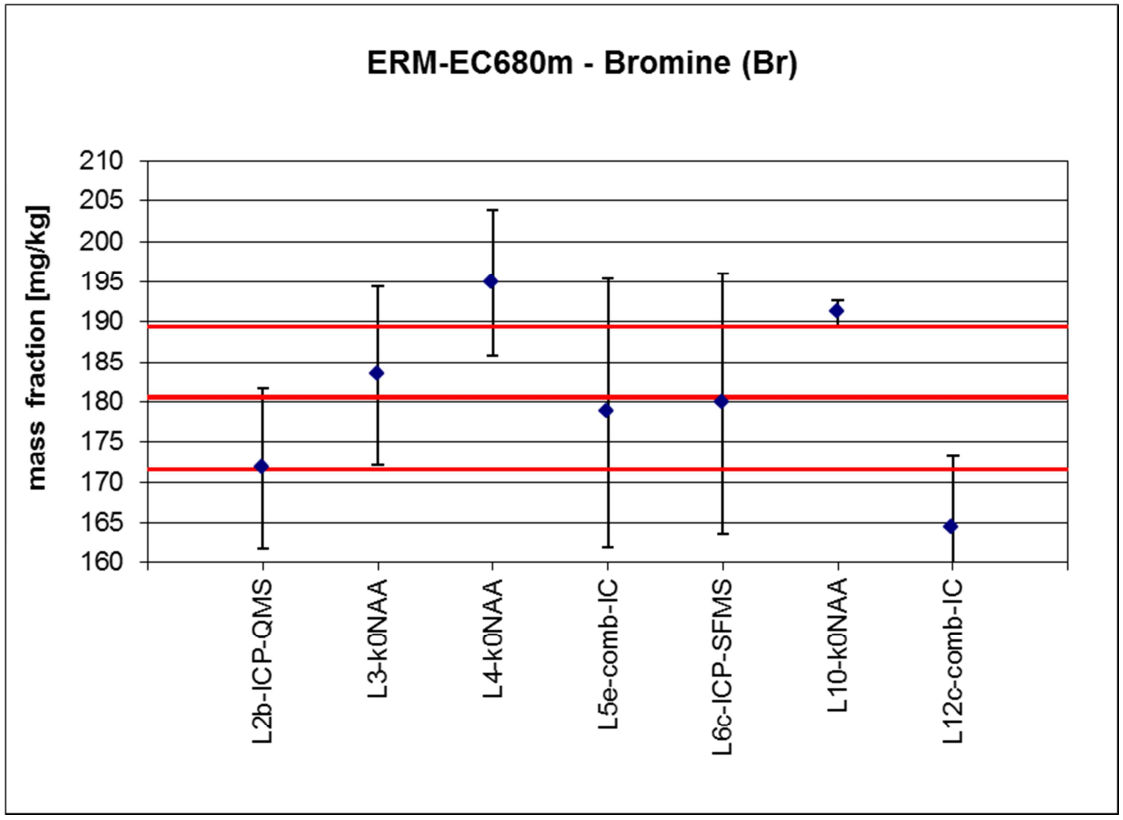
Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2-ICP-QMS	5.1	4.8	5.0	4.6	4.8	5.0	4.883	14.3
L3-k0NAA	4.38	4.33	4.29	4.26	4.34	4.63	4.372	6.4
L4-k0NAA	4.86	4.69	4.75	4.55	4.74	4.68	4.712	4.8
L5c-ICP-AES	4.63	4.24	4.20	4.57	4.62	4.22	4.412	34
L5d-ICP-SFMS	4.73	4.83	4.87	4.43	4.50	4.52	4.646	21.1
L6b-ICP-SFMS	4.62	4.73	4.72	4.36	4.81	4.84	4.680	7.46
L8a-ETAAS	5.84	5.66	6.11	5.30	5.28	4.61	5.466	18.8*
L8b-ICP-QMS	4.2	4.5	4.5	4.4	4.3	4.5	4.400	13.6
L8c-ICP-AES	5.38	5.21	5.30	5.25	5.60	5.01	5.292	9.45
L10-k0NA	4.86	4.6	4.58	4.61	4.6	4.59	4.640	8.41
L11-ICP-AES	5.1	4.8	4.6	4.9	4.4	5.1	4.817	12*
L12a-ICP-QMS	4.74	4.82	4.93	4.39	4.53	4.60	4.667	8.4
L12b-ICP-AES	4.64	4.22	5.03	4.20	4.26	4.47	4.469	14.4
Data not used for certification								
L1a-ICP-QMS	3.9	3.5	3.4	3.4	3.1	2.8	3.350	40
L1b-ICP-AES	4.6	5.8	4.2	4	5.7	36	4.860 *	40*
L9-ICP-AES	6.88	4.19	< LOD	< LOD	< LOD	< LOD	n.a.	n.a.

* average and standard deviation calculated without the outlier (replicate 6)



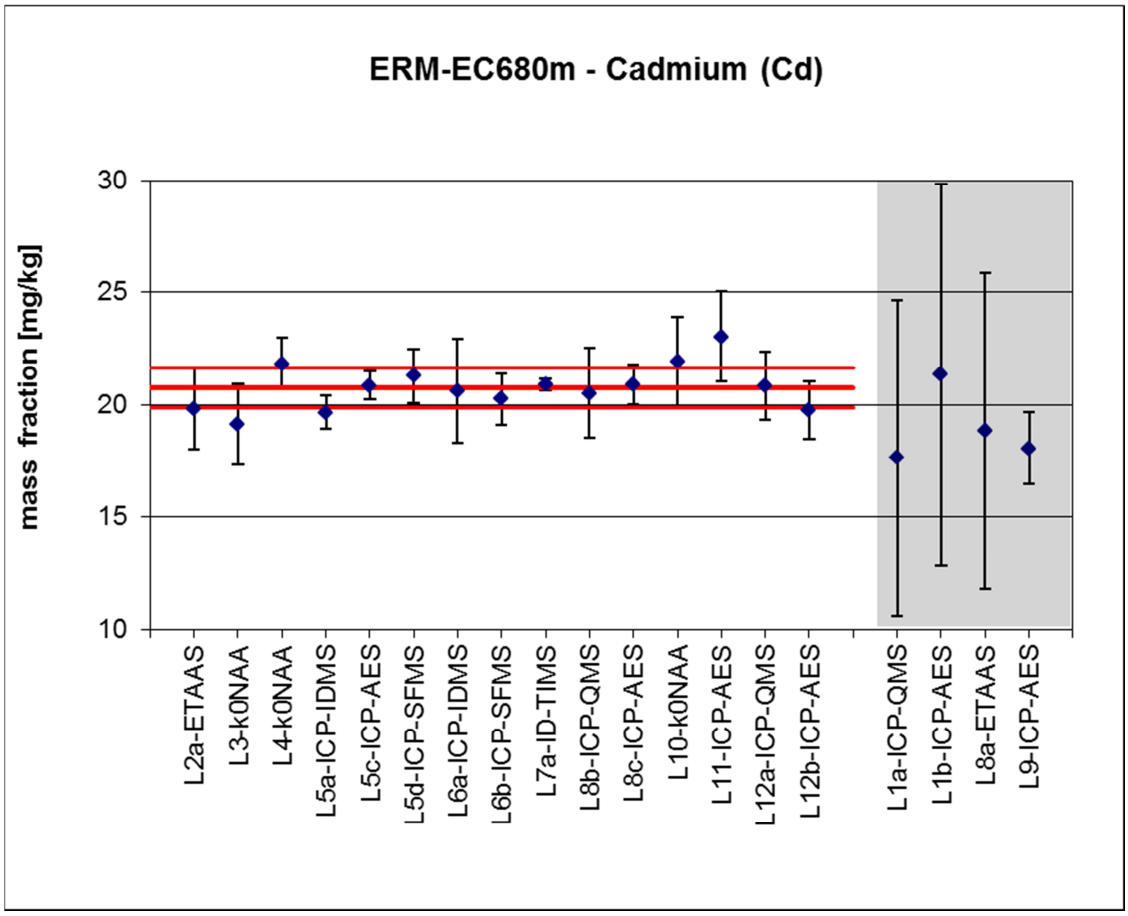
Br-Bromine

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2b-ICP-QMS	170	170	180	180	160	170	171.7	5.8
L3-k0NAA	185	182	181	186	181	185	183.3	6.1
L4-k0NAA	193	194	195	203	194	189	194.8	4.6
L5e-comb-IC	170	185	177	179	187	174	178.7	9.4
L6c-ICP-SFMS	166	184	178	183	190	178	179.8	9.0
L10-k0NAA	197	186	193	190	194	187	191.2	0.8
L12c-comb-IC	160	167	162	161	164	172	164.3	5.4



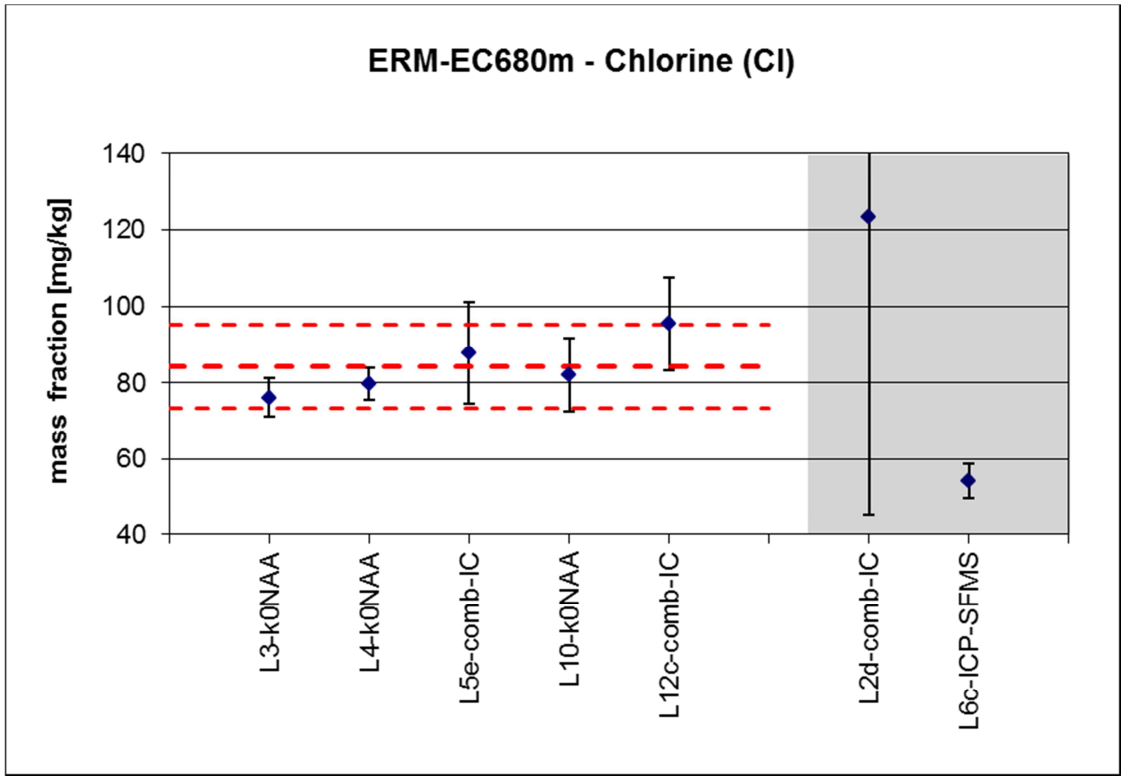
Cd-Cadmium (results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-ETAAS	21	19	19	22	19	19	19.8	9.1
L3-k0NAA	18.9	18.5	19.2	18.7	18.9	20.6	19.1	9.4
L4-k0NAA	22.0	21.7	22.3	22.4	21.3	21.4	21.8	5.3
L5a-ICP-IDMS	19.2	20.2	19.9	19.3	19.7	19.6	19.7	3.7
L5c-ICP-AES	19.8	20.5	20.4	20.4	21.5	22.5	20.9	3.0
L5d-ICP-SFMS	21.8	21.7	22.0	20.5	20.5	21.1	21.3	5.6
L6a-ICP-IDMS	19	20.2	21.2	20.5	20.3	22.4	20.6	11.2
L6b-ICP-SFMS	20.1	20.6	19.5	19.7	20.7	20.9	20.3	5.6
L7a-ID-TIMS	20.8	20.3	22.1	20.3	20.9	21.0	20.9	1.3
L8b-ICP-QMS	19.9	20.7	20.7	20.4	20.2	21.1	20.5	9.8
L8c-ICP-AES	21.2	20.4	21.1	20.7	22.0	20.1	20.9	4.3
L10-k0NAA	23.1	21.4	21.8	21.7	22.2	21.3	21.9	9.1
L11-ICP-AES	23.3	23.2	22.7	22.9	22.9	23.2	23.0	8.7
L12a-ICP-MS	20.7	21.3	22.1	19.9	20.4	20.6	20.8	7.3
L12b-ICP-AES	19.5	20.3	20.7	19.3	19.8	19.0	19.8	6.5
Data not used for certification								
L1a-ICP-QMS	20	19.4	16.9	18.2	15.5	15.7	17.6	40.0
L1b-ICP-AES	21.1	21.1	21.5	21	21.8	21.5	21.3	40.0
L8a-ETAAS	19.1	24.5	22.7	17.6	12.4	16.7	18.8	37.6*
L9-ICP-AES	17	17.6	17.6	18.3	19.7	18.2	18.1	8.8



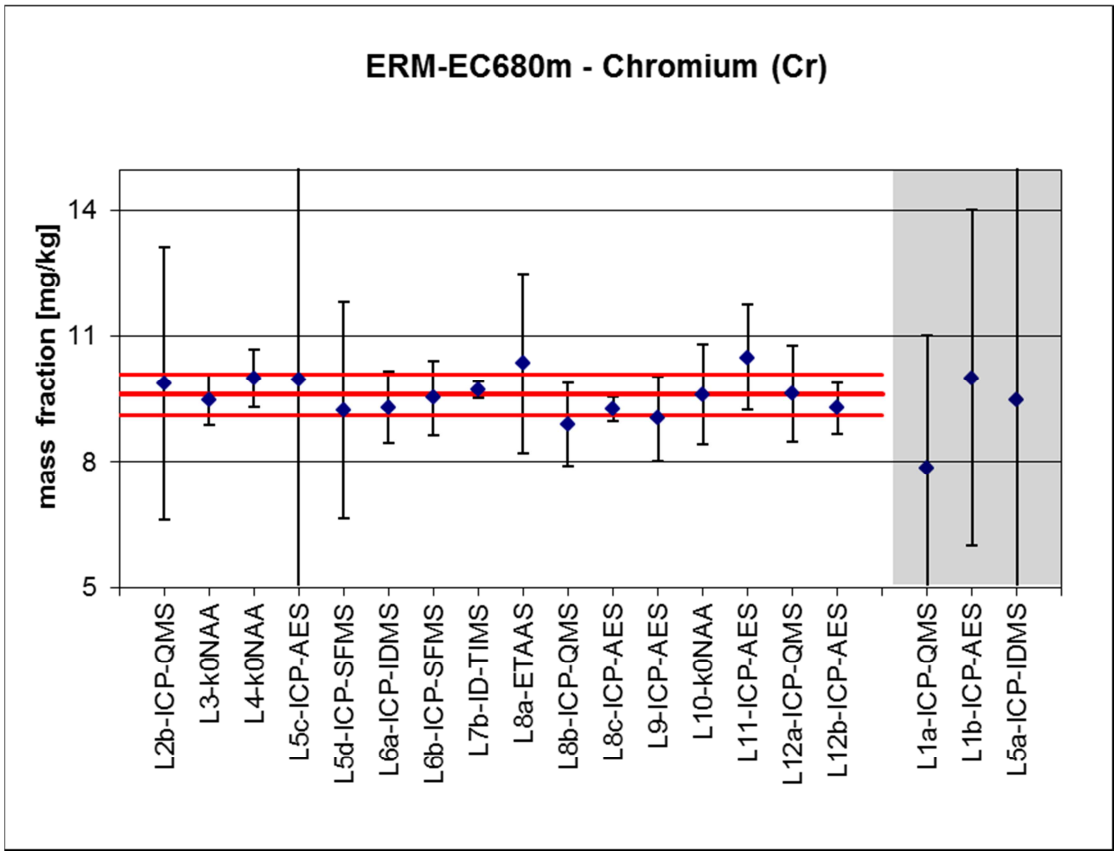
Cl-Chlorine (indicative value only) (results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L3-k0NAA	77.1	76.6	75.8	77.6	75	75.2	76.2	6.6
L4-k0NAA	82.3	79.9	76.0	81.1	78.7	79.9	79.7	5.3
L5e-comb-IC	90.3	87.7	89.6	93.1	86.7	79.4	87.8	15.0
L10-k0NAA	78.7	85.8	78.5	79.7	87.4	82.8	82.2	11.5
L12c-comb-IC	90.5	92.1	102.4	88.8	102.7	96	95.4	12.6
Data not used for certification								
L2d-comb-IC	140	140	130	120	100	110	123.3	63.3
L6c-ICP-SFMS	55.9	57	51.4	54.1	55.1	51.7	54.2	8.4



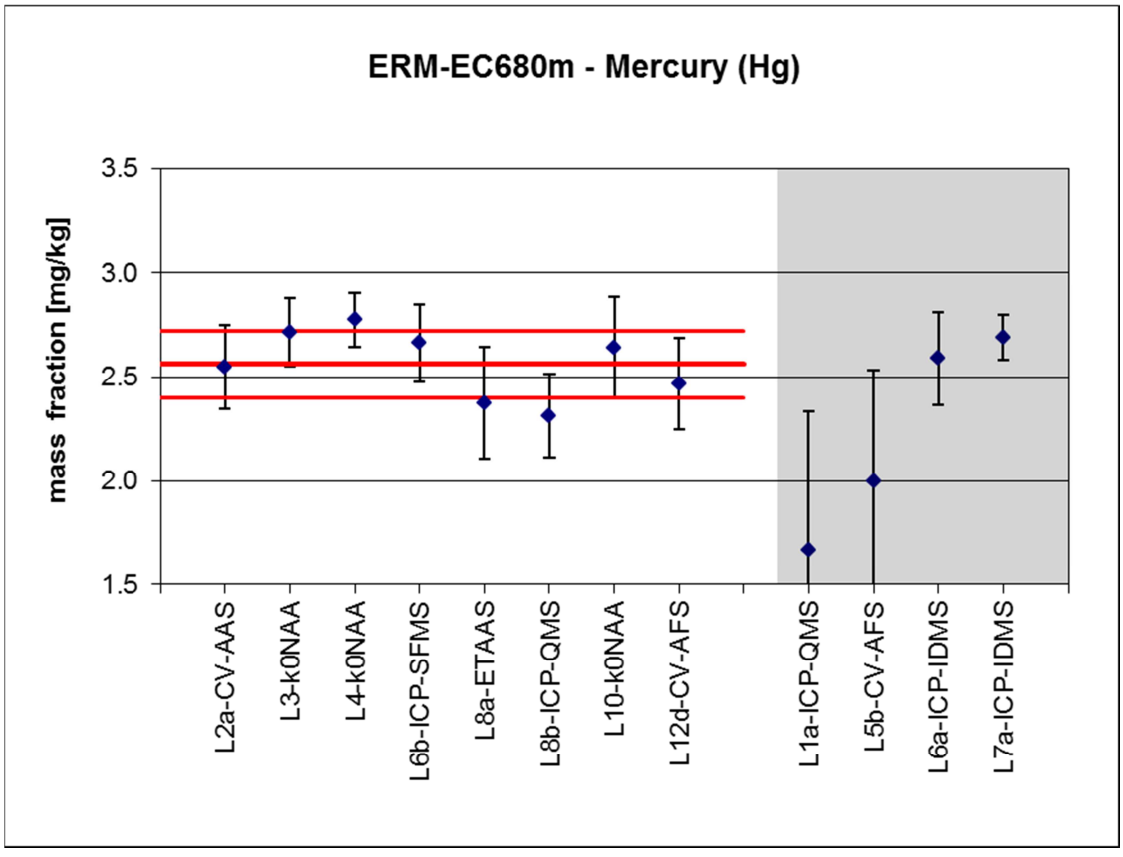
Cr-Chromium(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2b-ICP-QMS	10	10	9.8	9.9	9.8	9.8	9.88	33.0
L3-k0NAA	9.48	9.33	9.35	9.48	9.31	9.9	9.48	6.3
L4-k0NAA	10.00	9.87	10.27	10.22	9.70	9.98	10.01	6.9
L5c-ICP-AES	8.71	9.87	9.14	10.52	10.66	10.90	9.97	87.3
L5d-ICP-SFMS	9.50	8.99	9.31	9.20	9.12	9.30	9.24	28.1
L6a-ICP-IDMS	8.92	8.84	9.25	9.33	9.55	9.99	9.31	9.1
L6b-ICP-SFMS	9.75	9.9	9.29	8.8	9.48	9.96	9.53	9.2
L7b-ID-TIMS	9.63	9.49	10.06	9.70	9.54	9.9	9.72	2.1
L8a-ETAAS	10.25	12.44	11.30	8.83	8.69	10.65	10.36	20.7*
L8b-ICP-QMS	8.6	8.9	9.1	9.1	8.9	8.8	8.90	11.2
L8c-ICP-AES	9.47	9.03	9.43	9.16	9.54	9.00	9.27	3.2
L9-ICP-AES	8.44	8.74	8.95	9.2	9.89	9.05	9.05	13.3
L10-k0NAA	9.66	9.11	9.66	9.24	9.51	10.5	9.61	12.4
L11-ICP-AES	10.9	10.5	10.2	10.3	10.5	10.6	10.50	12.0*
L12a-ICP-QMS	9.94	10.10	10.37	8.98	9.22	9.19	9.63	11.9
L12b-ICP-AES	9.16	9.46	9.83	9.05	9.28	9.01	9.30	6.6
Data not used for certification								
L1a-ICP-QMS	8.7	8.6	7.6	8.4	6.8	7.1	7.87	40.0
L1b-ICP-AES	9.7	10	10.4	9.8	10.4	9.8	10.02	40.0
L5a-ICP-IDMS	9.32	9.57	9.49	9.33	9.60	9.54	9.47	82.4



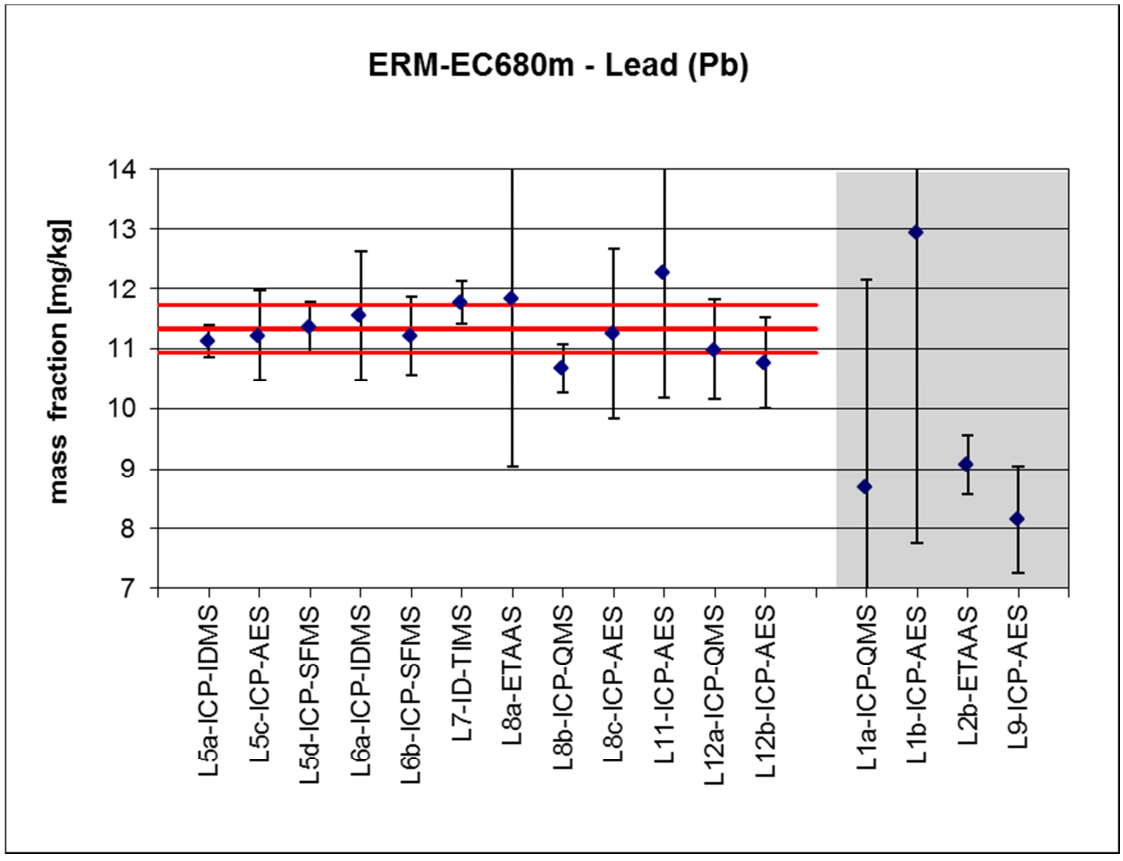
Hg-Mercury(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-CVAAS	2.5	2.6	2.6	2.6	2.5	2.5	2.55	7.8
L3-k0NAA	2.74	2.66	2.67	2.67	2.66	2.88	2.71	6.0
L4-k0NAA	2.82	2.75	2.85	2.79	2.65	2.79	2.77	4.7
L6b-ICP-SFMS	2.62	2.69	2.54	2.61	2.8	2.71	2.66	6.8
L8a-ETAAS	2.443	2.346	2.545	2.412	2.145	2.369	2.38	11.2*
L8b-ICP-QMS	2.3	2.5	2.3	2.3	2.3	2.2	2.32	8.6
L10-k0NAA	2.76	2.55	2.69	2.61	2.66	2.57	2.64	9.1
L12d-CV-AFS	2.399	2.634	2.553	2.33	2.445	2.449	2.47	8.8
Data not used for certification								
L1a-ICP-QMS	1.7	1.7	1.6	1.7	1.6	1.7	1.67	40.0
L5b-CVAFS	1.97	2.04	1.88	2.07	2.02	2.02	2.00	26.5
L6a-ICP-IDMS	2.48	2.78	2.49	2.65	2.59	2.54	2.58	8.5
L7a-ICP-IDMS	2.48	2.78	2.49	2.65	2.59	2.54	2.59	4.0
L6a-ICP-IDMS	2.48	2.78	2.49	2.65	2.59	2.54	2.59	8.5



Pb-Lead(results in the grey shaded part of the graph were not used for value assignment)

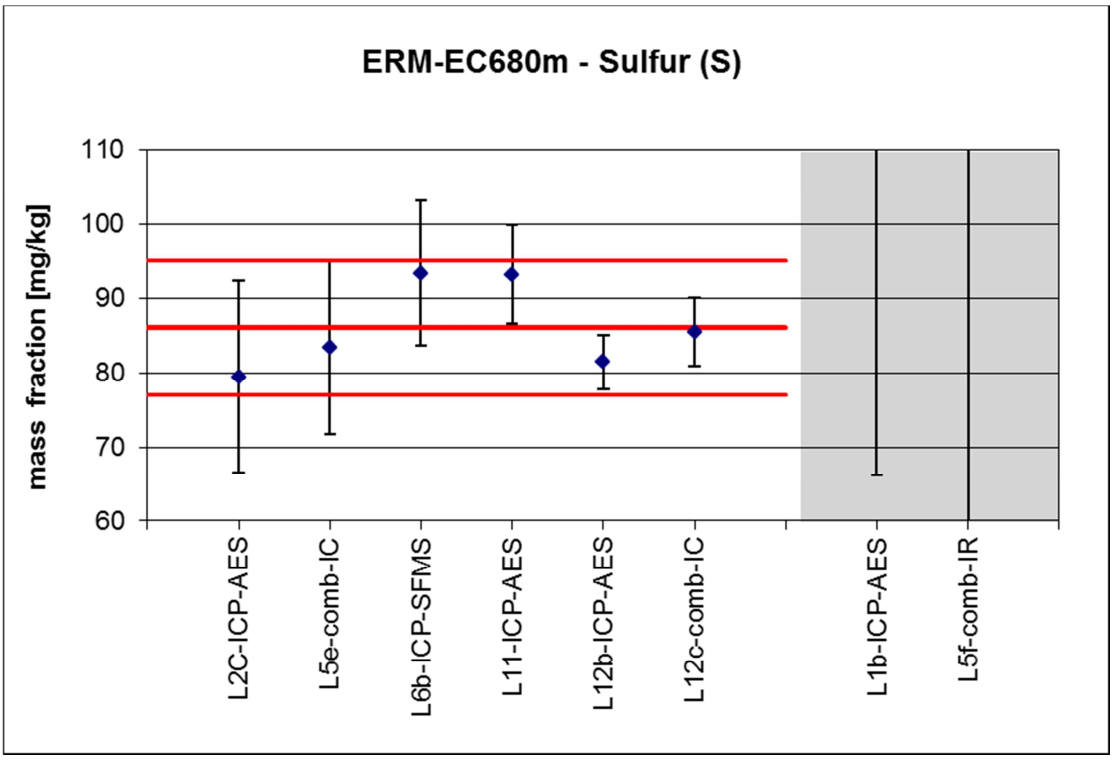
Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L5a-ICP-IDMS	10.9	11.5	11.3	10.8	11.2	11.1	11.1	2.4
L5c-ICP-AES	10.2	10.6	10.6	11.9	11.5	12.4	11.2	6.7
L5d-ICP-SFMS	11.3	11.3	11.5	11.7	11.2	11.2	11.4	3.7
L6a-ICP-IDMS	10.8	11.4	12	11.6	11.2	12.3	11.6	9.4
L6b-ICP-SFMS	11.4	11.5	11.2	10.6	11.4	11.2	11.2	5.8
L7a-ID-TIMS	12.2	11.5	11.8	12.4	11.3	11.5	11.8	3.1
L8a-ETAAS	12.8	11.8	11.4	11.3	12.9	10.8	11.8	23.6*
L8b-ICP-QMS	10	11	11	11	10	11	10.7	3.8
L8c-ICP-AES	11.4	10.8	11.4	11.2	11.8	11.0	11.3	12.6
L11-ICP-AES	12.5	12.6	12.2	12.0	12.0	12.3	12.3	17.1
L12a-ICP-QMS	10.9	11.2	11.6	10.4	10.8	10.9	11.0	7.6
L12b-ICP-AES	10.7	11.2	11.2	10.4	10.8	10.3	10.8	7.0
Data not used for certification								
L1a-ICP-QMS	9.5	9.4	8.3	9	7.8	8.1	8.7	40.0
L1b-ICP-AES	13.2	13.2	12.1	13.3	12.5	13.3	12.9	40.0
L2b-ETAAS	8.9	8.3	9.9	9.2	9.1	9	9.1	5.5
L9-ICP-AES	8.58	8.89	6.87	7.43	9.07	8.06	8.2	11.0



S-Sulfur(results in the grey shaded part of the graph were not used for value assignment)

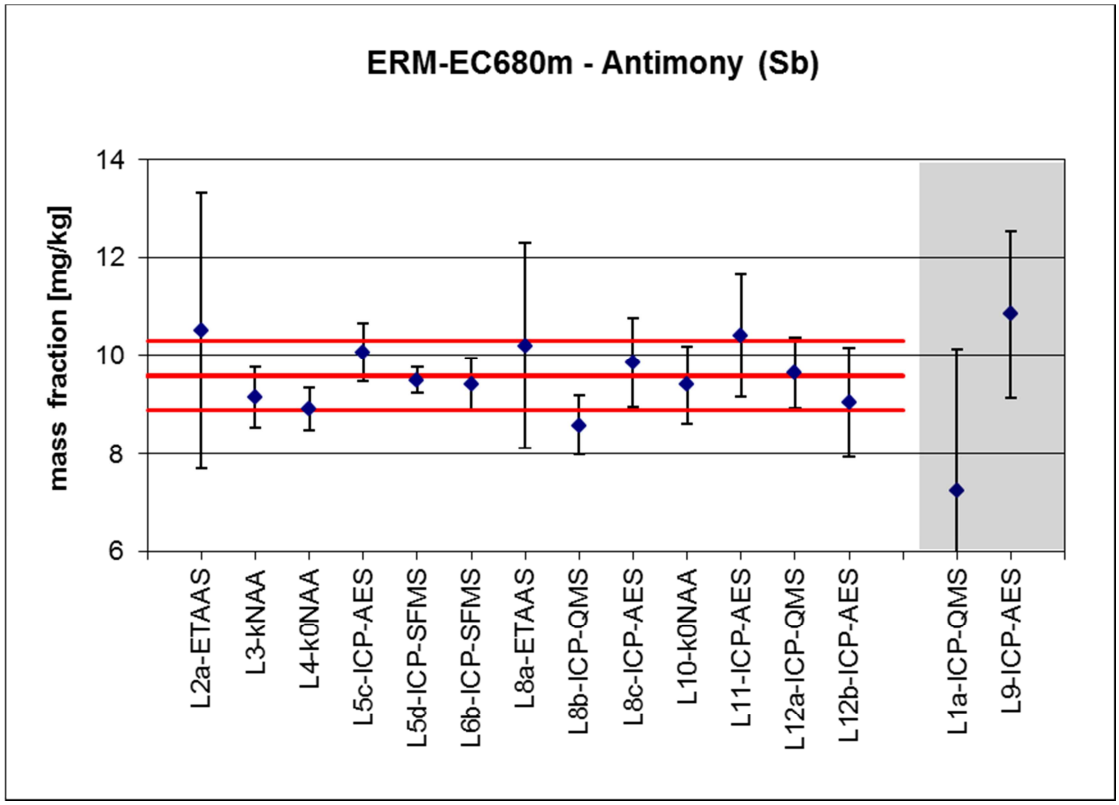
Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2C-ICP-AES	76	78	80	82	80	81	79.5	16.4
L5e-comb-IC	84.4	81.5	82.1	85.7	84.1	82.1	83.3	14.0
L6b-ICP-SFMS	88.1	95.8	92.9	97.9	87.2	98.6	93.4	10.5
L11-ICP-AES	93.6	92.8	89	94.8	93.9	95.4	93.3	7.1
L12b-ICP-AES	78.5	82.6	83.1	81.3	82.9	80.1	81.4	4.5
L12c-comb-IC	87.1	87	83.2	85.9	81.9	87.6	85.5	5.4
L1b-ICP-AES	89.2	104.7	94.2	94	169.6	401.7	110.3*	40.0
L5f-comb-IR	278	313	282	259	270	278	280.0	100.0

* Average calculated without the outlier on replicate 6.



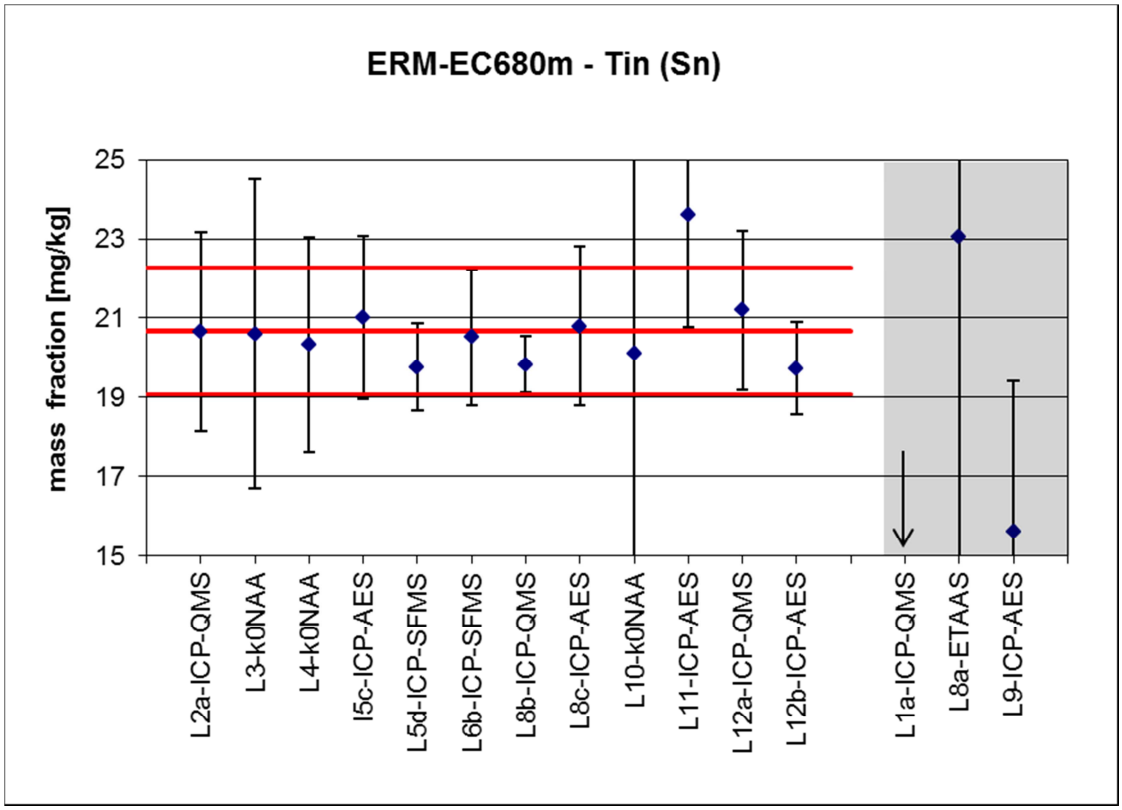
Sb-Antimony(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-ETAAS	11	10	11	10	11	10	10.5	26.7
L3-kNAA	9.22	9	9.04	8.98	9.02	9.63	9.1	6.6
L4-k0NAA	8.8	8.9	9.1	8.9	8.8	8.9	8.9	4.77
L5c-ICP-AES	9.1	9.4	10.1	10.0	10.9	10.8	10.1	5.8
L5d-ICP-SFMS	9.4	9.5	9.8	9.4	9.4	9.4	9.5	2.8
L6b-ICP-SFMS	9.74	9.35	9.24	9.06	9.45	9.68	9.4	5.52
L8a-ETAAS	11.2	9.5	12.1	8.6	10.7	9.0	10.2	20.4*
L8b-ICP-QMS	8.5	8.6	8.4	8.4	8.8	8.8	8.6	7.03
L8c-ICP-AES	10.5	9.5	9.8	9.9	10.1	9.2	9.8	9.15
L10-k0NAA	9.7	9.14	9.52	9.29	9.5	9.23	9.4	8.3
L11-ICP-AES	10.5	10.5	9.9	10.4	10.4	10.7	10.4	12.0*
L12a-ICP-QMS	9.6	9.9	10.2	9.2	9.5	9.5	9.6	7.5
L12b-ICP-AES	8.6	9.2	8.8	8.6	10.1	9.0	9.0	12.3
Data not used for certification								
L1a-ICP-QMS	7.1	7.8	8.3	6.5	6.5	missing	7.2	40
L9-ICP-AES	10	9.72	11.1	11.7	11.5	11	10.8	15.68



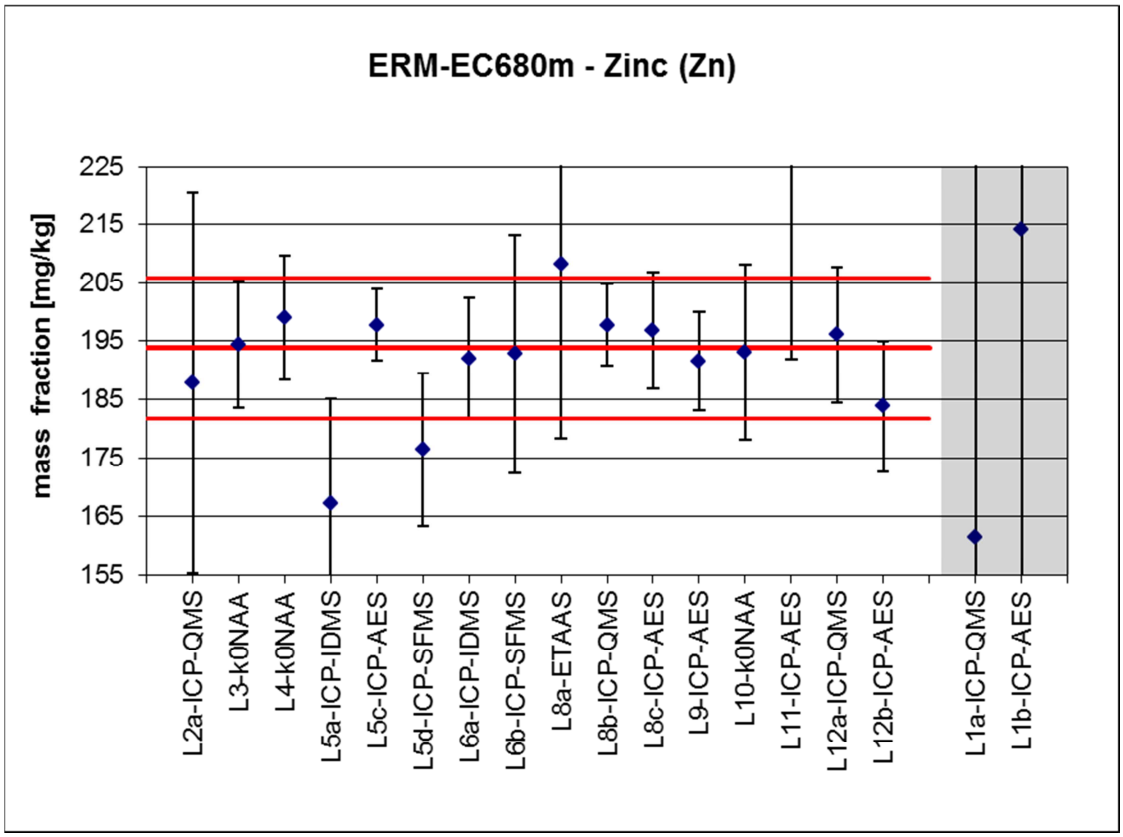
Sn-Tin(results in the grey shaded part of the graph were not used for value assignment)

3	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-ICP-QMS	21	20	21	21	21	20	20.7	12.1
L3-k0NAA	20.5	18.7	21.1	21	18.5	23.8	20.6	19.0
L4-k0NAA	20.311	20.063	22.083	20.518	18.521	20.465	20.3	13.4
l5c-ICP-AES	19.507	21.453	20.59	20.427	22.266	21.822	21.0	9.7*
L5d-ICP-SFMS	19.6908	19.3172	20.1261	20.2608	19.7136	19.4604	19.8	5.6
L6b-ICP-SFMS	21.5	19.4	20.3	19.7	21	21.2	20.5	8.3
L8b-ICP-QMS	19	20	20	20	20	20	19.8	3.5
L8c-ICP-AES	21.55	20.23	19.94	20.87	21.56	20.61	20.8	9.6
L10-k0NAA	18.8	21.7	20.6	15.6	20.6	23.4	20.1	27.4
L11-ICP-AES	24.4	24.4	23.8	22.8	23	23.2	23.6	12.0*
L12a-ICP-QMS	21.57	22.01	22.52	19.93	20.47	20.67	21.2	9.4
L12b-ICP-AES	19.59	20.17	20.54	19.33	19.82	18.9	19.7	5.9
Data not used for certification								
L1a-ICP-QMS	3.8	4.9	4.4	4	4.2	3.7	4.2	40.0
L8a-ETAAS	21.839	19.061	18.954	25.875	26.39	26.209	23.1	46.1*
L9-ICP-AES	15.1	10.2	15.7	18.9	18.3	15.5	15.6	24.3



Zn-Zinc(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-ICP-QMS	190	192	189	187	187	182	187.8	17.3
L3-k0NAA	197	191	191	192	193	203	194.5	5.6
L4-k0NAA	201	203	205	196	192	197	199.1	5.3
L5a-ICP-IDMS	157	178	165	163	175	165	167.2	10.8
L5c-ICP-AES	190	196	198	193	204	206	197.8	3.1
L5d-ICP-SFMS	178	173	173	182	176	177	176.4	7.4
L6a-ICP-IDMS	186	191	197	191	188	199	192.0	5.4
L6b-ICP-SFMS	192	203	185	183	202	192	192.8	10.6
L8a-ETAAS	217	212	183	212	200	226	208.2	14.4
L8b-ICP-QMS	195	197	199	199	193	204	197.8	3.5
L8c-ICP-AES	199	194	199	196	203	191	196.9	5.1
L9-ICP-AES	178	182	193	201	202	194	191.7	4.4
L10-k0NAA	197	192	195	191	194	190	193.2	7.8
L11-ICP-AES	227	228	221	227	226	227	226.0	15.0
L12a-ICP-QMS	197	200	204	187	193	195	196.1	5.9
L12b-ICP-AES	183	188	192	179	184	177	183.8	6.1
L1a-ICP-QMS	176	176	155	167	146	150	161.6	40.0
L1b-ICP-AES	210	214	212	210	216	222	214.2	40.0



European Commission

EUR 27572 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: **CERTIFICATION REPORT The Certification of the Mass Fractions of As, Br, Cd, Cr, Hg, Pb, S, Sb, Sn and Zn in Low-Density Polyethylene: ERM®-EC680m**

Author(s): Raquel Sanchez Romero, Thomas P.J. Linsinger

Luxembourg: Publications Office of the European Union

2015 – 52 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424

ISBN 978-92-79-53800-1

doi: 10.2787/255735

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new methods, tools and standards, and sharing its know-how with the Member States, the scientific community and international partners.

Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security, including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

LA-NA-27572-EN-N

Publications Office

doi:10.2787/255735

ISBN: 978-92-79-53800-1